

Amphiphilic mesoporous poly(ionic liquid) immobilized heteropolyanions towards efficient heterogeneous epoxidation of alkenes with stoichiometric hydrogen peroxide

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Abstract: Novel mesoporous poly(ionic liquid)s (MPILs) featuring pure polycationic framework and tunable hydrophobicity were synthesized through the free radical polymerization of alkylfunctionalized ionic liquids (ILs) and bis-vinylimidazolium salt. Phosphotungstic (PW) anions were firmly immobilized on these MPILs with high dispersion and density. The obtained catalyst was effective in the epoxidation of cis-cyclooctene with stoichiometric H_2O_2 , rendering the high yield (>98%) and remarkable H_2O_2 efficiency (>98%). The maximum turnover number (TON) and turnover frequency (TOF) arrived at 2375 and 685 h⁻¹, respectively. The catalyst can be facilely recovered by filtration and reused with stable activity. Various other alkenes can be also converted with high yields. The extraordinary performance was attributable to the pure ionic porous framework with enhanced hydrophobicity that not only provides strong cation-anion interaction towards the stable immobilized PW anions with high dispersion, but also enables the strong affinity of the catalyst with both the substrate and oxidant.

Introduction

Oxidation of organic compounds with hydrogen peroxide (H_2O_2) is a promising green and sustainable route to produce numerous valuable chemicals, attributable to the efficiency of this easily available oxidant with the by-product of sole H_2O .^[1-3] The transformation with high yield in the presence of only one equivalent of H_2O_2 relative to the substrate is especially appealing in the viewpoint of eco-friendly and atom-efficient process.^[4-6] Moreover, heterogeneous catalysts are preferable by considering the facile separation and reuse of the catalyst.^[3-5,7-9] Therefore, design of stable and efficient heterogeneous catalyst towards target reaction is highly desirable but still challenging in the oxidation with stoichiometric H_2O_2 .

Epoxides are valuable intermediates in industry and organic synthesis. Alkene epoxidation with H_2O_2 to produce epoxides is widely investigated as one of the basic reactions,^[4,10] with the application of a large number of homogeneous and heterogeneous catalysts including zeolites,^[11-12] metal oxides,^[13] polyoxometalates (POMs)^[14] and organic metal complexes.^[15]

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Supporting information for this article including the details of the additional experiment, characterizations and catalysis is given via a link at the end of the document.

POMs were extensively studied due to their high reactivity and selectivity, controllable structure, versatile acid/redox properties, strong persistence against oxidants and environmental compatibility.^[14,16-18] Many POMs-based catalysts have been developed for alkene epoxidation with H_2O_2 .^[14,19-21] For example, Ti-substituted phosphotungstate was active in the epoxidation of alkenes.[20] various Alkylimidazolium/alkylpyridinium octamolybdates acted as an efficient self-separating catalyst in the epoxidation of alkenes.^[21] Heterogenized POMs using imidazole functionalized silica,^[22] metal-organic frameworks (MOFs),^[23] metal oxide^[24] and so on were also constructed for this reaction. Among these POMs, phosphotungstic anion (PW) is a classical commercial Keggin-type POM and able to catalyze many organic oxidations, with the active oxygen-transfer species Venturello-Ishii $\{PO_4[WO(O_2)_2]_4\}^{3-}$ activated by H_2O_2 in the alkene epoxidation.^[25] Great deals of approaches are proposed to fabricate heterogeneous PW catalysts.^[9,22,26-29] However, most of these PW catalysts were carried out by using excessive H₂O₂ or alkene, and many of them still had the problemes such as low yield, inferior TON and potential leaching of active sites, particularly in the presence of stoichiometric H_2O_2 .^[9,19,26-29]

Immobilization of POM anions on a support is an efficient way to achieve heterogeneous POM catalysts, and the support chemistry significantly affects their activity and stability.^[8,30] Oxidation of organic compounds with H₂O₂ usually involves a water/oil reaction system; therefore, the heterogeneous catalyst should be amphiphilic with suitable hydrophilicity and hydrophobicity to deliver sufficient affinity towards the organic substrate in oil phase and oxidant (H₂O₂) in an aqueous phase.^[31-35] This requires the support having tunable wettability. Further, abundant porosity and strong interaction with active sites are necessary to achieve a high dispersion with good stability.^[29,36,37] Mesoporous poly(ionic liquid)s (MPILs).^[29,38] which are also named as porous poly(ionic liquid)s (PPILs)^[39,40] or nanoporous poly(ionic liquid)s (NPILs),^[37,41,42] are versatile supports to fulfill these requirements: 1) the porosity and chemical composition can be facilely adjusted;^[29,36,38-42] 2) the organic framework provides good organic compatibility;[36-42] 3) importantly, the ionic moiety in the skeleton endows strong cation-anion interaction for stable immobilization, having the advantage of ionic liquids (ILs) modified POM salts.^[29,37,39,40,42] Normally, the wettability can be tailored through the copolymerization of hydrophobic nonionic monomers and ILs,^[43] vet, this strategy will decrease the density of IL moieties in the framework, which may weaken the interaction of the support with the POM anions. Nonetheless, wettability manipulation of pure polycationic framework is difficult because of the inner hydrophilic nature of an ionic network.

In order to address this issue, herein, we reported the synthesis of a new kind MPIL through the copolymerization of a long carbon chain tethered IL [3-dodecyl-1-vinylimidazolium]Br (DIM) and rigid bis-vinylimidazolium salt [C₁DVIM]Br as the



cross-linker. Pure polycationic framework with tunable hydrophilicity and hydrophobicity was achieved by controlling the initial molar composition of IL monomers. High ionic density in these MPILs enabled the firmly immobilization of PW anions through a facile ion-exchange process. The supported PW anions presented enhanced hydrophobicity in a pure ionic framework, and therefore exhibited high activity in the epoxidation of cis-cyclooctene to 1,2-epoxycyclooctane with stoichiometric H₂O₂. Almost complete conversion was obtained, with high TON and TOF. The evaluation of the recycling performance and structure characterization of the reused catalyst revealed the high stability and good reusability. The scope was explored in the epoxidation of other alkenes. Various control samples were investigated to gain insight into the reaction. The affinity of the catalyst with the substrate and product was explored through zeta potential and adsorption.



Scheme 1. Preparation of PDD(x) and PW@PDD(x).

Results and Discussion

Catalysts preparations and characterization

Scheme 1 illustrates the synthetic procedure of MPILs PDD(x)and corresponding immobilized heteropolyanions PW@PDD(x)(x = 0.33, 1, 2 and 4; x was the initial molar ratio of DIM to $[C_1DVIM]Br$). The supports PDD(x) with different chemical composition were synthesized through the copolymerization of IL monomer [C1DVIM]Br and DIM by varying the initial molar ratio of these two kind IL monomers. All of them exhibited type IV nitrogen sorption isotherms, index of typical mesoporous structure (Figure S1A). The relatively wide pore-size distribution curves (Figure S1B) with the average pore sizes of 8-18 nm (Table 1) further revealed the existence of abundant mesopores. They had moderate surface area and pore volume (Table 1). CHN elemental analyses indicated that the [C1DVIM]Br/DIM molar ratio in the solid for each sample was very close to the one in the gel, reflecting a well copolymerization of these two monomers (Table S1). Further increasing the [C1DVIM]Br/DIM molar ratio to be x=6 led to a nonporous sample with the surface area lower than 0.5 m² g⁻¹. The self-polymerization of [C1DVIM]Br reached a large surface area, while the selfpolymerization of DIM gave a nonporous structure (Table S2). These phenomena suggest that [C1DVIM]Br plays an important role as the cross-linker in the pore formation. These PDD(x)samples possess pure polycationic networks, thus PW anions can be facilely immobilized through an ion-exchange process, offering PW@PDD(x) series with the PW loading amount of sorption about 50% (Table 1). PW@PDD(x) had the similar

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Figure 1. (A) N_2 sorption isotherms and (B) pore size distribution curves.

nitrogen isotherms to their parent supports (Figure 1), indicating the well-preserved mesoporosity. Compared with PDD(x), PW@PDD(x) possessed slightly decreased pore volume due to the occupation of the PW anions in the mesopores, which is further demonstrated by the decreased average pore size (Table 1).



Figure 2. SEM images of (A) PDD(4) and (B) PW@PDD(4); (C-F) Elemental mapping and (G) TEM images of PW@PDD(4).

SEM images (Figure 2A, B) of the typical samples PDD(4) and PW@PDD(4) demonstrated that both of them had irregular fluffy coral-shaped morphology and were composed of bulk granules with the particle size from tens of nanometer to more than hundred nanometer (Figure S2A, B). Actually, all these PW@PDD(x) samples possessed similar morphology (Figure S2C-E). Energy-dispersive X-ray spectrometry (EDS) elemental mapping analysis (Figure 2C-F) validated the immobilization of

Table 1. Textural properties.										
Sample	$S_{BET}^{[a]} (m^2 g^{-1})$	V _p ^[b] (cm ³ g ⁻¹)	D _{av} ^[c] (nm)	DIM: [C ₁ DVIM]Br ^[d] (mol/mol)	DIM Cont. ^[e] (mmol g ⁻¹)	PW ^[f] (wt%)				
PDD(0.33)	54	0.23	17.4	0.3 : 1	0.66	-				
PW@PDD(0.33)	83	0.17	8.4	0.3 : 1	0.29	56				
PDD(1)	53	0.32	24.2	0.8 : 1	1.35	-				
PW@PDD(1)	64	0.23	14.2	0.8 : 1	0.62	54				
PDD(2)	49	0.34	28.2	1.7 : 1	1.98	-				
PW@PDD(2)	48	0.16	13.6	1.7 : 1	1.07	46				
PDD(4)	31	0.24	30.6	3.4 : 1	2.27	-				
PW@PDD(4)	38	0.17	17.8	3.4 : 1	1.32	53				

[a] BET surface area. [b] Total pore volume. [c] Average pore size. [d] The molar ratio of DIM to [C1DVIM]Br calculated from CHN elemental analysis (Table S1). [e] The molar content of DIM in the solid. [f] The loading amount of PW anions measured by inductively coupled plasma (ICP).



Figure 3. (A) Water droplets on the surface; (B) TG curves, (C) FT-IR and (D) UV-vis and (E) 13 C MAS NMR spectra; (F) 31 P MAS NMR spectrum.

PW species with high dispersity. TEM image of PW@PDD(4) further revealed the morphology and porous structure (Figure 2G). XRD pattern of PW@PDD(4) showed an amorphous structure compared to $H_3PW_{12}O_{40}$ (HPW) (Figure S3), suggesting a highly dispersion of supported PW anions. This phenomenon differs from previous typical IL-POMs,^[9] PIL-POMs^[26] and POSS-POMs,^[27] in which a sharp peak was observable in 6-10° due to the formation of crystalline phase with a certain long-range ordered structure.

The IL monomer [C₁DVIM]Br is hydrophilic, while DIM with a long alkyl chain has hydrophobicity. Therefore the samples PW@PDD(x) with different content of DIM exhibited varied hydrophilic and hydrophobic properties. Immobilization of PW anions on PDMBr (self-polymerization of [C₁DVIM]Br) led to a

hydrophilic sample PW@PDMBr with the contact angle of 0° (Figure 3A). PW@PDD(0.33) with only low content of DIM presented a significantly enhanced hydrophobicity with the contact angle of 32°. Increasing the DIM content continuously enhanced the hydrophobicity of PW@PDD(*x*) series, and PW@PDD(4) with the highest DIM content gave the largest contact angle of 51° (Figure 3A). It should be noted that each PW@PDD(*x*) sample has almost the same contact angle as PDD(*x*), suggesting that the wettability was kept after loading of PW anions. This phenomenon shows that the copolymerization of hydrophilic and hydrophobic IL monomers is able to fabricate pure ionic framework with moderate hydrophobicity.

Additional characterizations were performed on PDD(4) and PW@PDD(4). Figure 3B displays the TG curves. Weight loss below ca. 100 °C was about 3-5%, due to desorption of physically adsorbed water. The starting decomposition temperature was ca. 270 °C, reflecting a high thermal stability. The drastic weight loss in the range of 270-350 °C is attributed to the degradation of the organic polymeric framework. The decomposition of the inorganic PW anions with the formation of P_2O_5 and WO_3 occurred at around 400 °C with slight weight lose.^[26] The weight loss was ca. 95% and 36% for PDD(4) and PW@PDD(4), respectively. As a result, PW content of PW@PDD(4) was about 55 wt% from TG result, similar to the value obtained from CHN elemental analysis (53 wt%).

Figure 3C illustrates the FT-IR spectra. PDD(4) exhibited a similar spectrum as PDMBr. The strong bands at 1636 and 1552 cm⁻¹ are attributed to C=N vibrations, indicating the existing of imidazole ring. The bands at 2920 and 2850 cm⁻¹ are assigned to -CH₃ and -CH₂ stretching vibrations, indicating the existence of alkyl chain in the polymeric skeleton. In the spectrum of PW@PDD(4), the characteristic vibration bands for the PW species appeared at 1080, 980, 895 and 808 cm⁻¹, assignable to the vibrations of P–O_a, W=O_d, W–O_b–W and W–O_c–W, respectively.^[9,14,22,28] The signals for the organic units of PW@PDD(4) are in accord with those of PDD(4), displaying the well-preserved polymeric framework. Several new peaks emerged on the spectrum of PW@PDD(4). The weak bands at 1105 and 1045 cm⁻¹ are branched peaks from the stretching P-O vibration at 1080 cm⁻¹, and the weaker signal at 950 cm⁻¹ is assigned to the split peak from the vibration of W^{VI}=O_d at 974 cm⁻¹. This phenomenon suggests the existence of an anion structure with lower symmetry than T_d symmetry of Keggin

 $[PW_{12}O_{40}]^{3-}$ anion, due to the strong interaction between the imidazolium cations and PW anions.^[9] Similar results were found in the FT-IR spectra of other PW@PDD(x) samples (Figure S4). The silent signal in the ESR spectra of PW@PDD(4) and PDD(4) (Figure S5) excluded the formation of partly reduced PW species, which was observed in the amino-tethered IL modified PW catalyst.^[9,44] The UV-vis spectra are illustrated in Figure 3D and S6. PW@PDD(x) and PW@PDMBr presented a wide adsorption band centered at 270 nm and a tail adsorption up to 400 nm, differing from the situation of the neat HPW and the support PDD(4). By contrast, IL modified PW salt [DIM]₃PW, which was obtained from the reaction of DIM with HPW, demonstrated similar UV-vis spectrum to the one of the neat HPW. In the spectrum of HPW, the strong and wide signals from 240 to 400 nm are attributed to the oxygen-tungsten charge transfer absorption bands for the Keggin anion.^[45] The imidazolium cations are strong electron-withdrawing groups that will cause significant inductive effect when they interact with the PW anions.^[22,46] Thus, apparent blue shift was found in the UVvis spectrum of IL or PIL modified POM anions. The stronger interaction responds to the more blue shift. Significant blue shift in the UV-vis spectra of PW@PDD(x) reflects a much strong cation-anion interaction that accouts for highly dispersed PW anions on the pure polycationic framework.

Table 2. Epoxidation of <i>cis</i> -cyclooctene with $H_2O_2^{[a]}$.								
Entry	Catalyst	Yield ^[b] (%)	Sel. ^[c] (%)	TON ^[d]	TOF ^[e] (h ⁻¹)	E _{hp} ^[f] (%)		
1	none	<1	-	-	-	<1		
2	$H_3PW_{12}O_{40}$	2	81	32	8	2		
3	PDD(4)	<1	-	-	-	<1		
4	PW@PDD(0.33)	75	>99	1225	306	74		
5	PW@PDD(1)	84	>99	1403	351	84		
6	PW@PDD(2)	87	>99	1465	366	86		
7	PW@PDD(4)	92	>99	1528	382	93		
8 ^[g]	PW@PDD(4)	>98	>99	>1119	>280	>98		
9 ^[g,h]	PW@PDD(4)	96	>99	1093	273	96		
10 ^[g,i]	PW@PDD(4)	30	>99	343	685	30		
11 ^[j]	PW@PDD(4)	70	>99	2375	594	69		
12	PW@Poly(DIM)	43	>99	726	182	43		
13	[DIM]₃PW	4	88	70	18	4		
14	[DIM] ₂ HPW	5	89	87	22	5		
15	[DIM]H ₂ PW	4	86	67	17	4		
16	PW@PDMBr	28	>99	460	115	28		
17	PW@SBA-15	5	85	85	21	5		
18	PW@SiO ₂	3	83	51	13	3		
19	PW@PDMBr-AM	30	>99	482	121	30		
20	PW@PAD-6	8	>99	132	33	8		
21	PW@PAD-2.5	77	>99	1297	324	77		

[a] Reaction conditions: *cis*-cyclooctene (5 mmol), H₂O₂ (5 mmol, 30 wt%), methanol (2 mL), catalyst (PW anions: 0.06 mol% with respect to substrate), 333 K, 4 h. [b] Yield of 1,2-epoxycyclooctane. [c] Selectivity of 1,2-epoxycyclooctane. [d] TON = mol products / mol (PW anions). [e] TOF = TON / reaction time (h). [f] E_{hp} (H₂O₂ efficiency) = [mol products / mol (consumed H₂O₂)] × 100. [g] Catalyst (0.09 mol% PW). [h] Yield and selectivity determined by ¹H-NMR spectroscopy using pyridine as the external standard. [i] 0.5 h. [j] Catalyst (0.03 mol% PW).

¹³C and ³¹P NMR spectra were measured. PDD(4) and PW@PDD(4) demonstrated almost the same ¹³C NMR spectra (Figure 3E), further approving the preservation of the polymeric framework during the ion exchange process. The peaks at 30 and 14 ppm come from the methylene (CH₂) and terminal methyl (CH₃) moiety of dodecyl in the DIM unit, respectively. The peaks at 42, 51 and 56 ppm are attributed to the alkyl groups of [C1DVIM]Br.^[38] Wide strong peaks around approximately 125 ppm are ascribed to the C4 and C5 carbon atoms in imidazole ring. The C2 atom in the imidazole ring corresponds to the single peak at 138 ppm.^[47] All of these signals prove the polymeric networks. The ³¹P NMR spectrum of PW@PDD(4) (Figure 3F) showed three signals at -15.5, -12.8 and -11.9 ppm. By contrast, the neat HPW normally presents only one peak at -15.6 ppm.^[22,46] Such phenomenon confirms the strong intermolecular electronic interaction between the imidazolium cations and PW anions that distorts the symmetry of PO₄ structure,^[22,46] in line with the FT-IR and UV-vis results.

Catalytic activities in the epoxidation reaction

PW@PDD(x) series were applied as heterogeneous catalysts in the epoxidation of alkenes with stoichiometric H₂O₂. The catalysis evaluation began in the epoxidation of the probe substrate cis-cyclooctene by using methanol as the solvent (Table 2). The spontaneous reaction in the absence of a catalyst gave a low yield below 1% (Table 2, entry 1). Neat HPW and support such as PDD(4) were inactive in the reaction, with much low yield of 2% (entry 2) or <1% (entry 3). PW@PDD(x)effectively catalyzed the epoxidation of cis-cyclooctene to 1,2epoxycyclooctane (entry 4-7). Only small catalyst dosage afforded high yields, resulting remarkable TON and TOF. The yield increased with the DIM content in the catalyst. Almost complete conversion (>99%) was achieved over PW@PDD(4) with highest DIM content and maximum hydrophobicity, rendering the highest yield of >98% (entry 8) with the TON of >1119 and TOF of >280. The yield was further confirmed by a ¹H-NMR experiment in this condition (entry 9, Figure S7). It is the first time to reach the efficient epoxidation of *cis*-cyclooctene with stoichiometric H₂O₂ by using a PW catalyst. Table S3 lists the previous heterogeneous catalysts in the epoxidation of ciscyclooctene with stoichiometric H₂O₂. Compared to these catalysts, PW@PDD(4) exhibited not only high yield but also remarkable TON/TOF values. Particularly, the TON/TOF values of PW@PDD(4) were larger than the ones of other PW-based catalysts (TON: 20-648, TOF: 4-162 h⁻¹) as well as the catalytic "Pickering" emulsions of nanoparticles [C12]3[PW12O40] (TON: 95, TOF: 158 h⁻¹). The TON/TOF values of PW@PDD(4) were also superior to or at least comparable to those best heterogeneous W-based catalysts (TON: 30-650, TOF: 7-188 h⁻¹). Noticeably, H_2O_2 efficiency (E_{hp}) reached a maximum value of >98% and the catalyst can be reused without deactivation and leaching, which were rarely achieved by these previous heterogeneous catalysts in the case of stoichiometric H₂O₂ (Table S3).

Figure 4 depicts the activity of PW@PDD(4) under different reaction conditions by changing the reaction time, catalyst dosage, solvent amount and type. The yield increased rapidly in the initial reaction stage, with TOF as high as 685 h^{-1} within the first 0.5 h (Figure 4A, Table 2, entry 10). Complete conversion

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was achieved at 4 h. Figure 4B displays the influence of catalyst dosage. Small amount catalyst (0.03 mol% PW) offered a yield of 70% with ultra-high TON of 2375 (entry 11). High catalyst dosage of 0.09 mol% PW caused a high yield of >98%. Further increasing the catalyst dosage resulted in a slight decrease of the yield, due to the deep oxidation of the product.^[48] The influence of the solvent amount is depicted in Figure 4C. The solvent-free reaction gave a yield of 70%, while moderate amount methanol (2 mL) led to the highest activity. A liquid-liquid-solid triphasic reaction system was formed by using 2 mL methanol as the solvent, because such a low amount of methanol is unable to completely dissolve the organic phase of *cis*-cyclooctene. Excessive solvent leads to a liquid–solid



Figure 4. Influences of (A) reaction time, (B) catalyst dosage, (C) the amount of methanol and (D) solvent type on the epoxidation of *cis*-cyclooctene with H_2O_2 catalyzed by PW@PDD(4). (A) Kinetic curves of the fresh and recovered catalyst after 1st run (dotted line: the hot filtration result). For each figure there was a specific parameter changed. The selectivity in each case was >99%. Reaction conditions: *cis*-cyclooctene (5 mmol), H_2O_2 (5 mmol, 30 wt%), methanol (2 mL), catalyst (0.09 mol% PW), 333 K, 4 h.

heterogeneous catalysis system but with a diluted concentration of the substrate, and thus reduced the activity.^[9] Figure 4D displays the activity of PW@PDD(4) in different solvents. PW@PDD(4) was insoluble in all cases and exhibited different catalytic activities. Low polar solvents such as chloroform, dichloroethane, ethyl acetate and dimethyl carbonate (DMC) resulted in inferior activity. The immiscibility of these solvents to H₂O₂ in a liquid–liquid–solid triphase reaction system hindered the contact of alkene with the oxidant, and therefore caused low activity.^[26] High yields were achieved by using high polar solvents such as methanol, acetonitrile, acetic acid and ethanol. These solvents have good miscibility to both alkene and oxidant, which are beneficial to the mass transfer.^[9,27] Among them, methanol led to the excellent catalytic performance in this reaction due to its nature of protonic solvent with moderate polarity.^[9]

For comparison, various control catalysts were prepared (their structure information is displayed in Figure S2, S8 and Table S1, S2). The self-polymerization of DIM led a nonporous catalyst

PW@Poly(DIM) with a surface area of 4 m² g⁻¹. This catalyst presented a yield of 43% (Table 2, entry 12), lower than the ones of PW@PDD(x) due to two disadvantages. On the one hand, the cation-anion interaction on PW@Poly(DIM) is weaker than the one on PW@PDD(x), as demostrated by the UV-vis analysis. The strong cation-anion interaction benefits active PW anions (details are seen in the section of "Insight into the reaction"). On the other hand, the low surface area of PW@Poly(DIM) is also disadvantageous for the dispersion and accessibility of PW anions. In this context, the abundant porosity of PW@PDD(x) is able to pomote the immobilization and dispersion of PW anions. Therefore, the abundant mesoporosity with moderate surface area is important for this reaction by enhancing the mass transfer and the dispersion of PW anions. [DIM]₃PW, [DIM]₂HPW and [DIM]H₂PW are typical heteropolyanion-based IL salts and exhibited a terrible yield of 4%, 5% and 4%, respectively (entry 13-15), due to their nonporous structure and the weak cation-anion interaction. PW@PDMBr containing no DIM monomer in the skeleton offered a low activity with the yield of only 28% (entry 16), apparently revealing the important role of hydrophobic long alkyl chain in the DIM mojeties. This result is in agreement with the fact that the high DIM content in PW@PDD(x) catalysts is related to the extraordinary activity. The reason can be attributed to that the increased hydrophobicity endows the catalyst with better surface wettability and thus enhances the interfacial interaction and mass transfer. Two other common supports of mesoporous silica SBA-15 and porous silica gel (SiO₂) were used to load HPW with the similar loading amount to the one of PW@PDD(4). The obtained catalysts PW@SBA-15 and PW@SiO₂ exhibited much low activity (entry 17 and 18), further revealing the advantage of MPIL as the support of PW anions to reach high performance.

For further comparison, various other MPILs, which were synthesized by using alkyl-tethered ILs with different carbon chain lengths of 2, 4, 8, 16 and 18 in the alkyl groups, were used as the supports of PW anions to generate PW@PDX(1) series (X= E, B, O, H and C₁₈) (their structure information is displayed in Figure S9-12 and Table S1, S4). Normally, alkyl group will improve the hydrophobicity and longer alkyl group responds to higher hydrophobicity. Therefore, the hydrophobicity of PW@PDX(1) increased with the elongation of the carbon chain length in IL monomers (Figure S12). All of these PW@PDX(1) samples exhibited higher activity than PW@PDMBr, due to the increased hydrophobicity (Table S5). Yields by usina PW@PDE(1) and PW@PDB(1) were 43% and 72%, respectively. This is attributed to that short alkyl group only slightly enhances the hydrophobicity. Long carbon chain can provide sufficient hydrophobicity. Therefore the PW@PDX(1) series obtained from the long alkyl group modified ILs demonstrated similar activity. These results additionally reveal that the wettability of MPIL supported PW anions becomes a vital factor for the activity in the epoxidation of *cis*-cyclooctene.

In order to clarify the influence of the polymeric framework and the hydrophobicity, PW anions were immobilized on mesoporous ionic copolymers of PAD-2.5 and PAD-6, which were the copolymerization of [3-aminoethyl-1-

vinylimidazolium]Br (AVIMBr) and divinylbenzene (DVB) with different IL content (their structure information is displayed in Figure S13 and Table S2).^[49] PDMBr-AM, copolymerization of AVIMBr and [C1DVIM]Br, was also synthesized and employed as the support of PW anions. The activity of the obtained catalysts PW@PDMBr-AM, PW@PAD-2.5 and PW@PAD-6 are listed in Table 2. Activity of PW@PDMBr-AM (30%, Table 2, entry 19) was similar to the one of PW@PDMBr, suggesting that amino-functionalization only slightly affect the activity. PW@PAD-6 with low IL content had a high hydrophobicity with the contact angle of 114° (Figure S13A), but gave a very low yield (8%, entry 20) in the reaction. The contributor can be assigned to that super-hydrophobicity obviously decreases the affinity of oxidant H₂O₂ towards the catalyst. PW@PAD-2.5 with high IL content has moderate hydrophobicity with the contact angle of 55° (Figure S13B), similar to the one of PW@PDD(4). However, the yield over PW@PAD-2.5 was only 77% (entry 21), far from the one (92%, entry 7) over PW@PDD(4) under the same condition. Such comparison clearly demonstrates the specialty of the pure polycationic framework with enhanced hydrophobicity to achieve highly efficient PW anions.

The reusability of PW@PDD(4) was verified in the epoxidation of *cis*-cyclooctene under optimum conditions. After reaction, the catalyst was facilely recovered by centrifugation and reused. In a six-run recycling test, stable high activity was observable (Figure 5A), revealing the well reusability. Further, comparison between the recovered PW@PDD(4) after 1st run and the fresh one was carried out in more detail throughout the reaction time course (Figure 4A). No deactivation was observable even at the initial reaction stage, further confirming the stability. A hot filtration experiment was carried out by stopping the reaction at 1 h with a yield of 60%, followed by removal of the solid catalyst. The yield was kept unchanged with the reaction of the filtrate solution going on (Figure 4A). No leached W species in the filtrate was determined by ICP, excluding the possible leaching of PW



Figure 5. (A) Reusability of PW @PDD(4) in the epoxidation of *cis*-cyclooctene with H_2O_2 . Reaction conditions: *cis*-cyclooctene (5 mmol), H_2O_2 (5 mmol, 30 wt%), methanol (2 mL), catalyst (0.09 mol% PW), 333 K, 4 h. (B) N₂ sorption isotherm and the corresponding pore size distribution curve (inset), (C) SEM image and (D-G) elemental mapping images of recovered PW@PDD(4) after 6th run.

anions. All of these observations prove the heterogeneous nature and stable reusability of PW@PDD(4). The recovered PW@PDD(4) after 6th run showed almost same structure and high dispersion of PW species as the fresh one (Figure 5B-G, Table S2), which accounts for such stability. Particularly, the recovered PW@PDD(4) after 6th run exhibited the same FT-IR spectrum as the recovered one after 1st run, although both of them had a slight variation from the fresh one. The initial signals at 950 and 895 cm⁻¹ for the vibrations of W=O_d and W-O_b-W presented a red shift to ca. 944 and 883 cm⁻¹ in the spectra of the recovered catalysts (Figure S14), suggesting the strengthened cation-anion interaction and distortion of PW species.^[50] The absence of the band at *ca.* 840 cm⁻¹ for v(O-O)precludes the degradation of intramolecular W-O-W into peroxo-bridged tungsten oxides.^[25,44] This phenomenon indicates that though slight distortion of PW anions occurred after 1st run, the catalyst becomes stable and can be reused without deactivation.

The scope of PW@PDD(4) was investigated by using other alkene substrates of cyclohexene, *cis*-3-Hexenol, bipentene and norbornene. Moderate to high yields were reached over these alkenes (Table S6), reflecting the well substrate compatibility of PW@PDD(4) in the epoxidation reaction.

Insight into the reaction

The porosity and surface wettability are crucial for a heterogeneous catalysis, because they significantly affect the dispersion and accessibility of the active sites. The remarkable performance of PW@PDD(4) can be assigned to the porous network of pure polycationic framework with enhanced hydrophobicity.

On the one hand, such type ionic framework endows the high density of ionic sites, and therefore provides a strong interaction with the PW anions to achieve a high dispersion and stable immobilization. This is different from the ionic copolymers with low ionic density that will cause potential leaching of the immobilized PW anions due to the relatively weak cation-anion interaction.^[27,51] Previous IL-POM salts also generated strong cation-anion interaction; yet, they usually presented the low surface area, with most of the POM anions embedded in the bulk phase.^[8,9,34,44] The pure ionic porous network enables the high dispersion of the PW anions on the surface of the solid with a relatively large surface area, which behaves as one important contribution to the high performance. Further, this strong cationanion interaction also benefits high active PW anions. For



Figure 6. (A) Zeta potentials of various catalysts colloidal particles from emulsion with a solution of *cis*-cyclooctene in methanol (0.1 mol L^{-1}). (B) The adsorption of *cis*-cyclooctene and 1,2-epoxycyclooctane on various catalysts.

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example, the higher activity of PW@Poly(DIM) than the one of $[DIM]_3PW$ can be assigned to this strong interaction to improve the activity of PW anions, becuase they have the similar chemcial composition and porosity. PW@PDD(*x*) series demonstrated much strong cation-anion interaction, which is also one contribution to their high activity.

On the other hand, the appropriate hydrophobicity improves the activity by enhancing the affinity of the organic substrate towards the active sites. The activity variation of PW@PDD(x)series clearly demonstrated an apparent strengthening effect of the hydrophobicity, because they possess almost identical active sites and porosity. This is further reflected by the activities of the controls with different wettability such as PW@PDMBr, PW@PAD-n and PW@PDX(1) samples. The surface wettability normally dominates the affinity of the catalyst with the substrates, medium and products, especially in a liquid-solid heterogeneous catalytic system.^[27,34,43,52-55] The hydrophobic olefin substrate is easy to attach a hydrophobic solid surface than a hydrophilic one. Therefore. PW@PDD(4) with enhanced hydrophobicity exhibited high efficiency. In order to support such speculation, zeta potentials of PW@PDMBr and PW@PDD(x) were measured to reflect the affinity of the organic solute to the surface of a solid (Figure 6A). The lower zeta potential is linked to the stronger affinity.^[56] The zeta potentials of these catalysts were around 30 mV in methanol. Decreased zeta potential was



Figure 7. The illustrations of the supports in H_2O_2/cis -cyclooctene water-oil system: (A) PDMBr suspended in aqueous H_2O_2 layer and (B) PDD(4) appeared at the H_2O_2/cis -cyclooctene water-oil interface. The illustrations of the PW @PDD(4) in the reaction system (H_2O_2/cis -cyclooctene /methanol): (C) before stirring, (D) after stirring for 5 min, (E) after centrifugation. (F) Possible mechanism for the biphasic epoxidation of alkenes with amphiphilic catalyst PW @PDD(4).

observed in a cis-cyclooctene/methanol solution, reflecting the varied affinity of cis-cyclooctene with these solids in an order of PW@PDD(4)>PW@PDD(2)>PW@PDD(1)>PW@PDD(0.33)>P W@PDMBr.^[56,57] This is in line with the sequence of their hydrophobicity, suggesting that the increased hydrophobicity will accelerate the reaction by improving the affinity of the substrate. Adsorption capacity of substrate cis-cyclooctene and product 1,2-epoxycyclooctane was investigated to gain further insight into the influence of surface wettability (Figure 6B). The adsorption amount of cis-cyclooctene increased with the hydrophobicity by utilizing methanol/water (v/v=1.5/0.5, the simulation of the actual reaction environment after addition of H₂O₂) as the solvent. This indicates that the surface wettability greatly affects the adsorption step in this reaction, exhibiting the hydrophobicity strengthening effect. The adsorption of 1,2epoxycyclooctane was weak over these catalysts, suggesting that the enhanced hydrophobicity of PW@PDD(4) promotes the adsorption of reactant and still remains a strong resistance towards the product. Such adsorption behavior benefits the substrate adsorption and product leaving, and thus can accelerate the reaction. All of the above analyses reveal that inserting the $-C_{12}H_{25}$ chains can accelerate the reaction by improving the affinity of the reactant with the catalyst.

To further illustrate the impact of the surface wettability, Figure 7A and B compare the dispersion state of PDMBr and PDD(4) in a biphasic system containing aqueous H₂O₂ solution and *cis*-cyclooctene. Hydrophilic PDMBr located in the water, while PDD(4) with the enhanced hydrophobicity existed in the water/oil boundary. In the reaction system (Figure 7C-E), PW@PDD(4) was well dispersed in the whole reaction solution and led to a metastable emulsion under vigorous stirring, due to the amphiphilic nature of PW@PDD(4). After reaction, the catalyst can still be facilely separated by centrifugation (Figure 7E).

In terms of these phenomena, a probable reaction model is presented in Figure 7F. H_2O_2 in aqueous phase reacts with PW anions to generate the peroxo-tungstate complex $\{PO_4[WO(O_2)_2]_4\}^3$, the commonly recognized actual active sites for epoxidation.^[25] Then, the oxygen of $\{PO_4[WO(O_2)_2]_4\}^3$ inserts into the olefin in oil phase to produce the epoxide product. Regeneration of active sites is obtained through the additional reaction with H_2O_2 . Appropriate amphipathy brings the easy accessibility of the catalyst with both the hydrophobic substrate in oil phase and the hydrophilic oxidant in aqueous phase. High dispersion of the surface PW species endows the efficient utilization of the active sites to achieve ultra-high TON.

Conclusions

Long alkyl chain functional MPIL supported PW anions demonstrated remarkable performance in the epoxidation of *cis*-cyclooctene with stoichiometric H_2O_2 , delivering the high yield, TON/TOF and H_2O_2 efficiency. After reaction, the catalyst can be conveniently recovered and reused without deactivation and leaching. The special pure polycationic porous framework with enhanced hydrophobicity accounts for this remarkable performance: 1) such type network provides a strong interaction

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with PW anions to firmly immobilize PW anions with high dispersion; 2) the appropriate hydrophobicity improves the activity by enhancing the affinity of the active sites towards both the organic substrate and oxidant. These results suggest that the functional MPILs are promising supports towards highly

effective heterogeneous catalyst to fulfill the requirement of

Experimental Section

atom-efficient catalytic process.

Materials and methods

All reagents were of analytical grade and used without further purification. [3-butyl-1-methylimi- dazolium]Br ([C₄MIM]Br), [3-ethyl-1-vinylimidazolium]Br (EIM), [3-butyl-1-vinylimidazolium]Br (BIM), [3-octyl-1-vinylimidazolium]Br (OIM) were provided by Shanghai Cheng Jie Chemical Co. LTD. [3-aminoethyl-1-vinylimidazolium]Br (AVIMBr) was provided by Lanzhou Yulu Fine Chemical Co. LTD.

¹H- and ¹³C- nuclear magnetic resonance (NMR) spectra were collected on a Bruker DPX 500 spectrometer at ambient temperature by using dimethyl sulfoxide (DMSO) or deuterochloroform (CDCl₃) as the solvent and tetramethylsilane (TMS) as the internal reference. Solid state ¹³C and ³¹P magic-angle spinning (MAS) NMR spectra were recorded on a Bruker AVANCE-III spectrometer (9.4 T, 100 MHz for $^{\rm 13}{\rm C}$ nuclei and 161.996 MHz for ³¹P nuclei with a CP/MAS unit). Attenuated total reflection-Fourier transform infrared spectra (ATR-FTIR) were recorded on an Agilent Cary 660 instrument ranging from 4000 to 650 cm⁻¹. Solid UV-vis spectra were measured with a Shimadzu UV 2600 spectrometer and BaSO₄ was used as the internal standard. Elemental analyses were made with a CHN elemental analyzer Vario EL cube. Metal content was analyzed by a OPTMA 20000V inductively coupled plasma (ICP) spectrometer. Scanning electron microscopic (SEM) images and energy-dispersive X-ray spectrometry (EDS) elemental mapping analysis were obtained on a Hitachi S-4800 fieldemission scanning electron microscope. Transmission electron microscopy (TEM) analysis was carried out on a JEM-2100 (JEOL) electron microscope operating at 200 kV. The nitrogen sorption isotherms and pore size distribution curves were tested at 77 K on a BELSORP-MINI analyzer. The samples were degassed at 363 K to a vacuum of 10⁻³ Torr before analysis. Thermogravimetric (TG) analysis was achieved on an STA409 instrument in dry air atmosphere at a heating rate of 10 °C min⁻¹. The surface wettability was studied by measuring the static water contact angles (WCA) through the pure water drop method on a DSA-100 contact angle goniometer under ambient conditions. XRD patterns from 5 to 50° (0.2° s⁻¹) were collected on a Smart Lab diffractmeter from Rigaku equipped with a 9 kW rotating anode Cu source at 45 kV and 200 mA. ESR spectra were recorded on a Bruker EMX-10/12 spectrometer at X-band.

Materials synthesis

Bis-vinylimidazolium salt [C₁DVIM]Br was prepared according to the literature.^[38] ¹H-NMR (500 MHz, DMSO, TMS) for [C₁DVIM]Br (Figure S15): δ (ppm) = 5.54 (d, 1H, -CH), 6.08 (d, 1H, -CH), 6.88 (m, 1H, -CH₂), 7.47 (d, 1H, -CH), 8.35 (d, 2H, -CH), 9.99 (d, 1H, -CH).

[3-dodecyl-1-vinylimidazolium]Br (DIM) was synthesized in a flask. *N*-vinylimidazole (4.71 g, 0.05 mol) and bromododecane (12.5 g, 0.05 mol) were dissolved in ethanol (20 mL), and then stirred at 80 °C for 48 h under nitrogen (N₂) atmosphere. After reaction, the solvent was removed by distillation. The solid product was washed with anhydrous diethyl ether and dried under vacuum at 60 °C for 12 h. Other IL monomers of [3-

hexadecyl-1-vinylimidazolium]Br (HIM) and [3-octadecyl-1-vinylimidazolium]Br (C $_{\rm 18}{\rm IM}$) were synthesized similarly.

 $^{1}\text{H-NMR}$ (500 MHz, CDCl₃, TMS) for DIM (Figure S16): δ (ppm) = 0.82 (t, 3H, –CH₃), 1.24 (m, 18H, –CH₂), 1.89 (m, 2H, –CH₂), 4.36 (m, 2H, –CH₂), 5.34 (d, 1H, –CH), 5.97 (d, 1H, –CH), 7.26 (d, 1H, –CH), 7.45 (d, 1H, –CH), 7.94 (d, 1H, –CH), 10.70 (d, 1H, –CH).

 $^{1}\text{H-NMR}$ (500 MHz, CDCl₃, TMS) for HIM (Figure S17): õ (ppm) = 0.88 (t, 3H, –CH₃), 1.30 (m, 26H, –CH₂), 1.95 (m, 2H, –CH₂), 4.41 (m, 2H, –CH₂), 5.40 (d, 1H, –CH), 6.01 (d, 1H, –CH), 7.30 (d, 1H, –CH), 7.52 (d, 1H, –CH), 7.94 (d, 1H, –CH), 10.77 (d, 1H, –CH).

 $^{1}\text{H-NMR}$ (500 MHz, CDCl₃, TMS) for C₁₈IM (Figure S18): δ (ppm) = 0.88 (t, 3H, –CH₃), 1.30 (m, 30H, –CH₂), 1.96 (m, 2H, –CH₂), 4.41 (m, 2H, –CH₂), 5.41 (d, 1H, –CH), 6.00 (d, 1H, –CH), 7.28 (d, 1H, –CH), 7.51 (d, 1H, –CH), 7.87 (d, 1H, –CH), 10.90 (d, 1H, –CH).

MPIL samples PDD(*x*) (*x* was the starting molar ratio of DIM to $[C_1DVIM]Br$, *x*=0.33, 1, 2 and 4) were synthesized through the free radical polymerization of $[C_1DVIM]Br$ and DIM, in which the mixture of IL $[C_4MIM]Br$ and a small amount of water was used as the solvent (Scheme 1). Typically, PDD(4) was synthesized as follows. $[C_1DVIM]Br$ (0.3 g), DIM (1.14 g), $[C_4MIM]Br$ (6 g), H_2O (1.0 mL) and 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AIBA) (0.03 g, 10 wt% with respect to $[C_1DVIM]Br$) were placed in a reaction tube. Subsequently, the mixture was stirred for at least 2 h until achieving a homogeneous transparent solution. The polymerization occurred statically at 100 °C for 24 h under N₂ atmosphere. After reaction, the solidified composite was washed with deionized water and ethanol and then dried under vacuum at 60 °C for 12 h. For comparison, various other MPILs were prepared similarly through the free radical polymerization of target monomers (details were found in the Supplementary Experimental).

Heteropolyanions supported ionic copolymers PW@PDD(*x*) were synthesized by the anion-exchange of PDD(*x*) with phosphotungstic acid (Scheme 1). Typically, PDD(4) (0.2 g) was dispersed in 30 mL deionized water, followed by the addition of an aqueous solution (30 mL) containing 1.0 g HPW. The resulting mixture was stirred at room temperature for 72 h. The solid was separated by filtration, washed with water and ethanol, and then dried in a vacuum at 60 °C for 12 h. The white sample (0.38 g) was got as PW@PDD(4). Other PW supported MPILs were prepared with the similar procedure by using target support. POM based ionic salt [DIM]₃PW, [DIM]₂HPW and [DIM]H₂PW were prepared through the reaction of DIM with HPW. PW@Poly(DIM) was synthesized by the anion-exchange of HPW with Poly(DIM), the polymer synthesized through the self-polymerization of DIM. PW@SBA-15 and PW@SiO₂ were prepared by wet-impregnation method. Details were provided in the Supplementary Experimental.

Catalysis assess

The catalytic performances were assessed in the epoxidation of the probe substrate *cis*-cyclooctene with hydrogen peroxide (H_2O_2) as the oxidant and methanol as the solvent. Typically, cis-cyclooctene (5 mmol), methanol (2 mL) and catalyst (0.024 g, 0.09 mol% PW anions with respect to substrate) were stirred in a reaction tube at 333 K for about 10 minutes, and then 30 wt% aqueous H2O2 (5 mmol) was added drop by drop for about 10 minutes under vigorous stirring. The reaction continued for 4 h with stirring and reflux. After reaction, the internal standard nheptanol was added and the resulting mixture was diluted with 10 mL methanol. The organic phase was collected by centrifugation and analyzed by gas chromatography (Agilent 7890B) equipped with a flame ionization detector and a capillary column (HP-5, 30m×0.25mm×0.25µm). The by-products were established by GC-MS (Agilent 7920A/5975). Conversion (based on substrate) = (mmol [converted substrate])/(mmol [initial substrate]) ×100%. Selectivity of epoxide = (mmol [converted substrate] - mmol [by-product])/(mmol [converted substrate]) ×100%. Yield (based on substrate) = (mmol epoxide)/(mmol initial substrate) $\times 100\%$. Other alkene substrates were evaluated similarly.

The reusability was assessed in a six-run recycling test. After each run, the catalyst was recovered by centrifugation, washed with ethanol, dried in vacuum and then charged into the next run. Hot filtration was carried out by stopping the reaction at 1 h. After filtration of solid catalyst, the filtrate was further stirred at the reaction temperature for another 3 h. The liquid phase was monitored by GC at the reaction time of 1, 1.5, 2, 3 and 4 h, respectively.

¹H-NMR experiments were performed in methanol-D4 (CD₃OD) with the same stoichiometry under the optimum conditions of PW@PDD(4). *Cis*-cyclooctene (5 mmol), CD₃OD (2 mL), PW@PDD(4) (0.024 g) and H₂O₂ (5 mmol) were mixed in a 25 mL reaction tube and stirred at 333 K for 4 h. After reaction, the external standards pyridine (5 mmol) was added and the solution was dried over anhydrous MgSO₄ for 12 h. The solid was separated by filtration and the liquid phase was analyzed by ¹H-NMR.

Zeta potential measurement

Typically, 10 mL methanol solution containing *cis*-cyclooctene (1 mmol) and 0.01 g solid sample were mixed in a 15 mL centrifuge tube. After ultrasound for 30 min, the upper colloid solution was tested by dynamic light scattering instrument (Malvern Instruments Zetasizer Nano ZS 90).

Adsorption of reactant and product

In a typical test, PDD(4) (0.1 g), adsorbate (10 μ mol) and methanol/water 1.5/0.5 mL (simulation of the actual reaction solution) were added in a tube and stirred vigorously at 298 K for 6 h. After the removal of the solid by filtration, the filtrate was analysed by GC. The adsorption amounts were calculated based on the variation of the adsorbate before and after adsorption.

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FULL PAPER

Long alkyl chain functional mesoporous poly(ionic liquid) featuring pure ionic porous framework with tunable hydrophobicity endowed firmly immobilized heteropolyanions with a high dispersion and density. As a results, the obtained amphiphilic catalyst exhibited high yield (>98%), remarkable H₂O₂ efficiency (>98%) and maximum turnover number (TON) up to 2375 in the alkene epoxidation with stoichiometric H_2O_2 .



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Amphiphilic mesoporous poly(ionic liquid) immobilized heteropolyanions towards efficient heterogeneous epoxidation of alkenes with stoichiometric hydrogen peroxide