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ARTICLE

Polyoxometalate-based phase transfer catalysis for liquid-solid organic reactions: a review

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Phase transfer catalysis combines the advantages of homogeneous and heterogeneous catalysts, therefore attracts ever-growing interest for environment-friendly sustainable processes. Polyoxometalates (POMs) are a class of molecular metal oxides showing numerous applications in various catalytic processes due to their unique acid/base and redox features. The tunable molecular structures of POM-anions and counter-cations bring about facile adjusting of POMs' physical and chemical properties including solubility, through which many POM-based phase transfer catalysts are fabricated, such as reaction-controlled, temperature-responsive and photo-sensitive phase transfer catalysts. This mini-review summarizes the recent progresses of POM-based phase transfer catalysis for liquid-solid organic reactions.

1. Introduction

Catalysis is the key technology in chemical processes for producing chemicals using homogeneous or heterogeneous catalysts.[1-7] Homogeneous catalysts usually exhibit high activity but have difficulty in separation, recovery and reuse. On the contrary, heterogeneous catalysts benefit facile separation and recycling but always suffer from inferior activity than homogeneous counterparts in most catalytic processes.[6-8] Alternatively, many efforts have been devoted to develop phase transfer catalysts (PTCs), which are homogeneous during the reaction and heterogeneous at the end of the reaction.[8-22] Traditionally, the term "phase transfer catalysis" is reserved for catalysts that mediate the transfer of inorganic ions from an aqueous phase into another organic phase where they bring about a reaction. Here, the described phase transfer catalysis is an extension of that classical item that is specifically referred to the catalyst phase change phenomenon from liquid to solid during an organic reaction. In other words, a PTC is solvable during the catalytic process, and becomes unsolvable after the catalysis to enable the precipitation of the catalyst from the reaction medium, such that the catalyst can be easily recovered for reuse.[10-14] Phase transfer catalysts combine the advantages of homogeneous

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catalysis (high activity, mass transfer elimination and well accessibility of substrates to catalytic active sites) and heterogeneous ones (facile separation and reusability), therefore have become a kind of promising catalysts accommodating the environment-friendly sustainable development.

Up to now, various PTCs have been designed by using polyoxometalates (POMs), polymers, ionic liquids (ILs), poly(ionic liquid)s (PILs), selenium and so on.[9-22] Among them, POMs are one of the most attractive candidates in this area. As a class of anionic metal-oxygen clusters, POMs can be varied facilely by changing compositions and structures in molecular level for adjusting acid, base, and/or redox properties, moreover, their porosity in nano-sized scale, and morphology in micrometer scope can also be modified.[6-14,23-32] Consequently, a great deal of POM-based catalysts, especially heteropolyanions (HPAs), have been developed and applied for numerous reactions, including esterification, transesterification, hydrolysis, Friedel-Crafts alkylation and acylation, Beckmann rearrangement, Knoevenagel condensation, Claisen-Schmidt condensation, and oxidations

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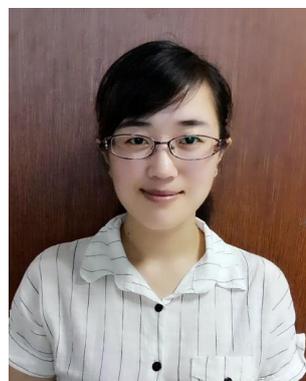
Qian Wang received his BS degree majored in Chemistry from Nanjing Tech University in 2014. Now she is pursuing her PhD career in Prof. Jun Wang's group in the same university. Based on ionic liquid polymers, her research interest focuses on the design and synthesis of ordered organic ionic frameworks enwrapping active sites such as polyoxometalates, as well as nanostructured carbons, and their applications in green catalysis and adsorption.

of alkanes, aromatics, olfins, alcohols, etc.[2-3,6-8,23-32] Normally, POMs are soluble in polar solvent and serve as homogenous catalysts, exhibiting high activity but suffering from the difficulty in catalyst recycling.[6-8] Insoluble POMs can be prepared by "solidification" with suitable cations or "immobilization" on porous carriers, fabricating numerous POM-based heterogeneous catalysts that benefit facile separation and reusability.[6-8] Nonetheless, POM-based heterogeneous catalysts are still limited by mass transfer, diffusion, and accessibility of the active sites, as met by various other heterogeneous catalysts.[1-8] In order to overcome above shortness, an alternative is to design POM-derived phase transfer catalytic systems by tuning solubility of POM-based catalysts. Many approaches have been proposed to construct POM-based PTCs towards specific requirements of different reactions. The most adopted strategy is to modify the cations of POMs with organic compounds such as ionic liquids, quaternary ammonium salts, oligomers and so on.[8-14,26-30] By choosing suitable cations and POM anions, reaction-controlled, temperature-responsive and photo-driven PTCs are fabricated from POMs for catalyzing various reactions, including esterification, transesterification, oxidative desulfurization, olefin epoxidation, hydroxylation of benzene and oxidation of alcohols.[8-14,26-30,33-36] A large number of reviews have been published for the synthesis, modification and application of POM-based materials, but none of them specialized on POM-based phase transfer catalysis previously. In this review, we summarize the recent process of POM-based phase transfer catalysis for liquid-solid organic reactions.

2. Discussion

2.1 The major type and application of POM-based PTCs

The phase transfer catalytic system is characteristic of that the solubility of the catalysts is sensitive to one response factor, thus homogeneous and heterogeneous states can be switched,

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achieving homogeneous catalysis of reaction and heterogeneous separation of catalyst (Figure 1).[9-14] According to difference of response factor in a phase transfer process, there are mainly two types of POM-based PTCs materials, the reaction-controlled and temperature-responsive ones in recentstudies,[9] in which the majority of POM-based PTCs are reaction-controlled PTCs.[9-14,23-30,33-36] The applications of POM-based PTCs focus on the acidic and oxidation liquid-solid organic reactions. The fact that no POM based PTCs has ever been employed in a basic reaction can be assigned to that the devolopment of POM-derived bases is still a difficult issue.[8,31] Oxidation reactions are most widely studied over POM-based PTCs, and one typical reaction is the epoxidation of various olefins, including linear terminal olefins, internal olefins, cyclic olefins, styrene and allyl chloride.[9,14,26,28] Recently, various

Figure 1 Schematically illustration of phase transfer catalytic systems.

newly designed POM-based PTCs are applied in other reactions such as esterification, transesterification, hydroxylation of benzene and oxidation of alcohols,[11,12,27] expending the scope of POM-based PTCs.

2.2 Synthesis and composition of POM-based PTCs

Generally, the POM based PTCs are fabricated through modification of POM anions with suitable organic cations.[9-14] The synthesis of POM base PTCs can be facilely achieved by a metathesis reaction or ion-exchanging process with the reaction between the organic compounds and the soluble POM materials in suitable solution.[8-14] The composition of cations and anions are both important for the activity and phase transfer process, therefore, the key step towards an efficient PTCs is to choose suitable cations and anions for certain reaction.[9-14,36-30] Besides, the solvents also affect the phase transfer properties and should be carefully selected for specific reaction.[37]

The anions of POM-based PTCs are mainly the Keggin type heteropolyanions (their crystal structure are seen in Figure 2) such as Venturello anion ($\{PO_4[WO(O_2)_2]_4\}^{3-}$),[9,34] phosphotungstic anion ($PW_{12}O_{40}^{3-}$),[10,11,26,27,30] silicotungstic anion ($SiW_{12}O_{40}^{4-}$),[26,38,39] phosphomolybdic anion ($PMo_{12}O_{40}^{3-}$),[39] double V-containing heteropolyanion ($PMo_{10}V_2O_{40}^{5-}$),[12] etc. Among them, $PW_{12}O_{40}^{3-}$ is the most studied POM anion.[10,11,26,27,30] Besides, various other POM anions are also utilized, including decatungstate ($W_{10}O_{32}^{4-}$),[36] heteropolyperoxotungstates ($PW_4O_{16}^{3-}$),[40-42] lacunary polytungstophosphate ($PW_{11}O_{39}^{7-}$),[43] octamolybdate ($Mo_8O_{26}^{4-}$)[14] and so on. Generally, the present studies mainly focus on the commercial heteropolyanions due to the facile availability and stability. The application of other non-commercial POM anions is limited due to the synthetic difficulty but more attractive because of the additional features and advantages derived from the tunable composition and molecular structure.
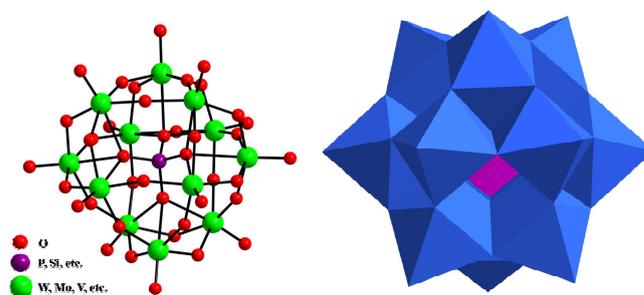
Figure 2 A) ball and stick and B) polyhedral crystal structure of a typical Keggin type heteropolyanion.

The organic cations can be quaternary ammonium salts, ILs, cationic surfactant and oligomers. Among them, the quaternary ammonium salts such as π-$C_5H_5N^+(C_{16}H_{33})_3$, $(C_{18}H_{37})_2(CH_3)_2N^+$, n-$C_{16}H_{33}(CH_3)_3N^+$ and p-$C_5H_5N^+C_{16}H_{33}$are the early widely used organic cations for POM based PTCs.[9,29,35,36,41-43] The obtained catalysts are mainly used in the oxidation reaction, especially the olefins epoxidation, in which the POM anions act as the active sites.[9,29,41] The utilization of ILs as the organic cations is able to create the active sites on either the organic cations or POM anions, providing additional potential functionalities.[11,12,14,30] For example, the acidic ILs can provide acidic properties for POM based PTCs that can be used in acidic phase transfer reactions such as esterification and transesterification.[11] Moreover, the redox properties of POM based catalysts can be finely adjusted by the IL cations through the special electronic behavior between the IL caions and POM anions, in other words, the intramolecular electron transfer between them.[44-46] As a result, the catalytic performance in oxidation reaction can be adjusted, which will improve the activity of POM based PTCs and expand their applications in wider fields.[12] Besides the quaternary ammonium salts and IL, some oligomers such as amine terminated polyisobutylene oligomer,[26] dendritic polyamidoamine (PAMAM) matrix[27] and poly ionic liquids

(PIL),[47] are also used to fabricate POM based PTCs. Though only several examples of PTCs derived from POM and oligomers have been reported, oligomers combining the advantage of polymers and organic compounds have become a potential promising candidate for POM based PTCs due to the versatile and facile adjustable composition and structure that will significantly affect the performance of the catalysts.

3 Reaction-controlled phase transfer catalysis

The exact concept of reaction-controlled POM-based PTCs was described by Xi for the first time in 2001.[9] The details are as follows. The catalyst itself is insoluble in the reaction medium, but can form soluble active species under the action of one of the reactants. The soluble active species subsequently react with another reactant to selectively generate the desired product, achieving the homogeneous catalysis. After the reaction, the first reactant is used up, causing the returning of the catalyst to its original composition or become unsolvable in the products. Therefore, the catalyst can precipitate from the reaction medium after the reaction, thus can be easily separated and reused. The above insoluble-soluble-insoluble process is controlled by one reactant, thus above POM-based PTCs are referred as reaction-controlled phase transfer catalysts.

Reaction-controlled POM-based PTCs are developed from the pioneer work of Venturello-Ishii catalytic system, a phase transfer system composed of POM anions like $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and phase transfer agents (mainly quaternary ammonium salts). The history of this type phase transfer catalysis can be traced back to 1980s. In 1983, Venturello et al. reported an effective catalytic system for epoxidation of olefins by H_2O_2 under phase-transfer conditions.[48] The catalytic system was resulted from $Na_2WO_4 \cdot 2H_2O$, 40% w/v H_3PO_4 and onium salt (Q^+X^-) with a molar ratio $PO_4^{3-}/WO_4^{2-}/Q^+$ of 5:2.5:1. In 1988, Venturello et al. fabricated the phase transfer catalytic system by adding H_2O_2 in the mixture of Na_2WO_4, H_3PO_4 and quaternary ammonium salts, the mixture of $(C_{18}H_{37})_2(CH_3)_2N$ (76%) and n-$C_{16}H_{33}(CH_3)_3N$ (24%).[49] The catalysts can efficiently epoxidize a variety of water-insoluble unactivated alkenes (internal or terminal, open-chain or cyclic, isolated or carrying diversified functionalities) under mild conditions. At the same time, Ishii et al. reported the phase transfer catalytic system using [π-$C_5H_5N^+(CH_2)_{15}CH_3)_3](PM_{12}O_{40})$, M=Mo or W, prepared from cetylpyridinium chloride and 12-molybdophosphoric acid or phosphotungstic acid. By using commercially available H_2O_2, the catalysts can efficiently catalyze the oxidation of olefins to epoxides, secondary alcohols to ketones, and α,ω-diols to lactones, as well as the oxidative cleavage of vic-diols and carbon-carbon double bonds of olefins.[50,51] Figure 3 presented the conceivable epoxidation path via peroxo-type intermediate catalyzed by heteropolyacids combined with cetylpyridinium chloride with H_2O_2, which was proposed by Ishii in 1988.[51] Deep investigations indicated that the active species in Ishii

system was same as the one in of Venturello, because the $PW_{12}O_{40}^{3-}$ was changed to be $\{PO_4[WO(O_2)_2]_4\}^{3-}$ in the epoxidation reaction. Therefore, the above two systems were named as Venturello-Ishii catalysis system and several related works were reported in 1990s.[52-56] Nevertheless, Venturello-Ishii system suffered from catalyst deactivation and difficulty in catalyst recovery arising from the insufficient precipitation of the catalyst after the reaction.
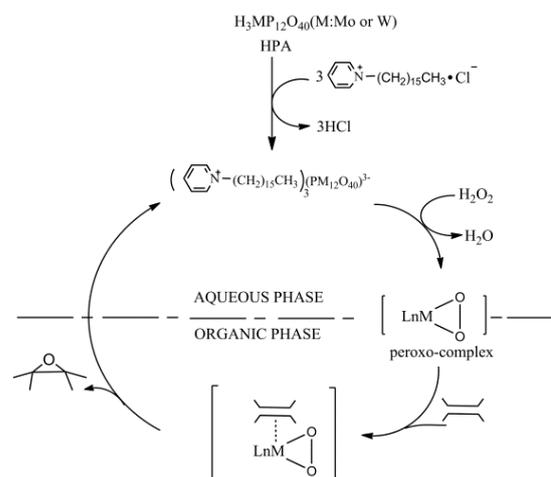
Figure 3 Conceivable epoxidation path via peroxo-type intermediate catalyzed by heteropolyacids combined with cetylpyridinium chloride with hydrogen peroxide. Reprinted with permission from ref. 51. Copyright (1988) American Chemical Society.

Based on the studies of Venturello-Ishii system, Xi et al. in 2001, reported a novel reaction-controlled phase-transfer system catalyzed by using quaternary ammonium heteropolyoxotungstates.[9] Figure 4 showed the catalytic mechanism of the catalyst [π-$C_5H_5N^+(C_{16}H_{33})_3][PO_4(WO_3)_4]$ for the epoxidation of propylene. The catalyst was powder-like solid and unsolvable in the reaction medium, but it dissolved slowly under the action of H_2O_2 in the epoxidation of olefins, which gradually changed the system from turbid to clear and subsequently leaded to homogeneous catalytic process. During the above soluble process, the initial $PW_4O_{16}^{3-}$ anions was changed to be $\{PO_4[WO(O_2)_2]_4\}^{3-}$ active species that can catalyze olefins to produce the epoxides. When the added H_2O_2 was used up, the catalyst precipitated gradually and the solution returned back to turbid, reflecting the completion of the reaction. Briefly, the catalyst manifested a solid-liquid-solid phase transfer process controlled by the reaction, thus is referred as the "reaction-controlled phase transfer catalyst". This catalytic system can be applied to the phase transfer catalytic epoxidation of most olefins (such as linear terminal olefins, internal olefins, cyclic olefins, styrene, and allyl chloride) and the oxidation of alcohols. After reaction, the catalyst can be filtered and reused just like a heterogeneous catalyst.
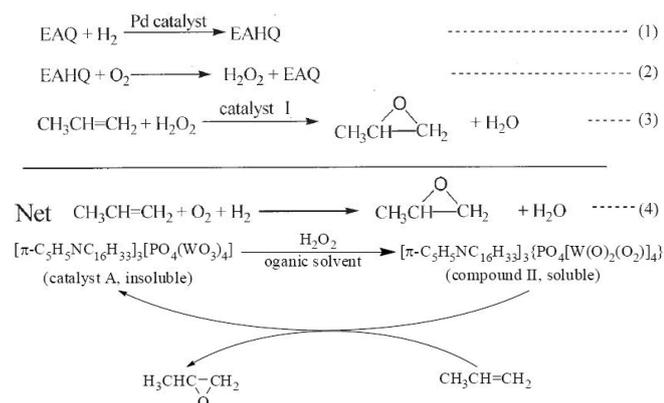
Figure 4 Epoxidation of propylene catalyzed by catalyst [π-$C_5H_5N^+(C_{16}H_{33})_3$][$PO_4(WO_3)_4$]. Reprinted with permission from ref. 9. Copyright (2001) the American Association for the Advancement of Science.

Since the discovery of above reaction-controlled phase transfer catalytic system, various studies were reported to explore the catalyst categories and their applications as well as the catalytic mechanism. In 2001, Sun et al. reported the epoxidation of olefins catalyzed by the reaction-controlled phase transfer catalyst [π-$C_5H_5N^+(C_{16}H_{33})_3$][$PW_4O_{16}$] with molecular oxygen and a recyclable reductant 2-ethylanthrahydroquinone, achieving good selectivity and high reductant utilization efficiencies (72.6-94.5%)for the epoxidation of cyclohexene, terminal olefins and allyl chloride.[57] In 2003, Zhou et al. applied the catalyst [π-$C_5H_5N^+(C_{16}H_{33})_3$][$PW_4O_{16}$] for the epoxidation of propylene with the *in situ* formed H_2O_2 generated by the oxidation of 2-ethylanthrahydroquinone (EAHQ) with molecular oxygen in the organic solvent. The selectivity for propylene oxide was 95% based on propylene and the yield was 85% based on 2-ethylanthrahydroquinone.[42] In 2004, Gao et al. performed a spectroscopic study (by FT-IR, Raman and ^{31}PNMR) on [π-$C_5H_5N^+(CH_2)_{15}CH_3)_3$][$PW_4O_{16}$]for catalyzing the epoxidation of cyclohexene with H_2O_2 in a biphase medium ($H_2O/CHCl_3$).[41] As shown in Figure 5, the results indicated that the insoluble catalyst could degrade into smaller soluble species, [$(PO_4)\{WO(O_2)_2\}_4$]$^{3-}$, [$(PO_4)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}$]$^{3-}$, and [$(PO_3(OH))\{WO(O_2)_2\}_2$]$^{2-}$ under the action of H_2O_2. The olefins were oxidized to epoxides with the active oxygen in the [$W_2O_2(O_2)_4$] structure unit of these soluble species, consequently producing the corresponding W-O$_b$-W (corner-sharing) and W-O$_c$-W (edge-sharing) bonds. The peroxo group [$W_2O_2(O_2)_4$] could be regenerated when these bonds reacted with H_2O_2 again. These soluble species lost active oxygen and then polymerized into larger compounds with these W-O-W bonds that then precipitated from the reaction solution after used up of H_2O_2. In 2004, Witte et al. reported the epoxidation of cyclooctene with H_2O_2 by using self-assembled $Na_{12}[WZn_3(ZnW_9O_{34})_2]$ in combination with a suitable phase

transfer agent such as methyltrioctylammonium chloride.[58] In 2004, Guo fabricated quaternary ammonium decatungstate catalyst [n-$C_{16}H_{33}(CH_3)_3N$]$_4W_{10}O_{32}$.[36] The catalyst presented reaction-controlled phase transfer phenomenon in the oxidation of alcohols with H_2O_2, including the oxidation of cyclohexanol to cyclohexanone, and hexanol and octanol to carboxylic acids. In 2005, Yang et al. reported reaction-controlled phase transfer epoxidation of styrene with H_2O_2 catalyzed by [($C_{18}H_{37}(30\%)+C_{16}H_{33}(70\%))N(CH_3)_3$]$_3$-[$PW_4O_{16}$].[37] The catalyst kept almost the same activity after two times recycling. In 2006, Chen et al. studied the structural change of [π-$C_5H_5N^+(C_{16}H_{33})_3$]$_3$\{$PO_4[WO_3]_4$\} during the selective oxidation of cyclopentene to glutaric acid with H_2O_2.[59] In 2007, Zhang el al. prepared the catalyst hexadecyltrimethyl ammonium heteropolyphosphatotungstate (n-$C_{16}H_{33}N(CH_3)_3$)$_3$[PW_4O_{16}] and applied it in the oxidation of secondary alcohols to ketones under solvent-free conditions by using aqueous H_2O_2 as oxidant, giving the yield of 92% and selectivity of 97%.[60] The catalyst could be reused without loss of selectivity. In 2008, Ding et al. synthesized a new tungsten-based polyoxometalate [p-$C_5H_5N(CH_2)_{15}CH_3$]$_3$[PW_4O_{32}], which could be used in a recyclable and environmentally benign catalytic system for the epoxidation of many kinds of alkenes by using 30% H_2O_2 as an oxidant and ethyl acetate as a solvent.[29] In 2008, Weng et al.
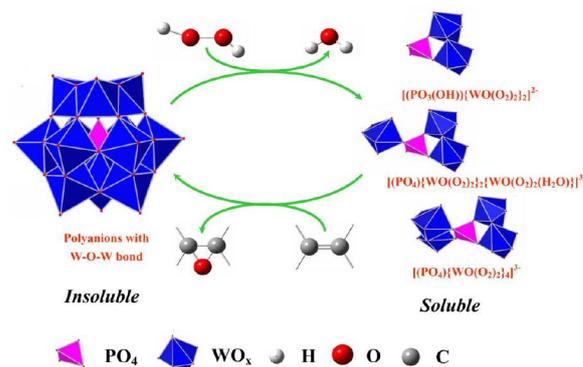
Figure 5 Reaction mechanism of the reaction-controlled phase transfer catalysis for cyclohexene epoxidation. Reprinted with permission from ref. 41. Copyright (2004) Elsevier.

prepared the lacunary POM-based reaction-controlled phase-transfer catalyst [$C_7H_7N(CH_3)_3$]$_7PW_{11}O_{39}$ that efficiently oxidized benzyl alcohol (BzOH) to benzaldehyde (conversion 95.8% and selectivity 99%) by using 35% aqueous H_2O_2 as oxidant.[61] The catalyst could be recycled three times without obvious decrease in activity. The recovery ratio was due to the maintaining of catalyst structure after the reaction.

Before 2009, the studies on the POM-based PTCs mainly focused on the application of quaternary ammonium salts as the phase transfer agents and H_2O_2 as the action agent to control the phase transfer process in the oxidation reactions such as olefines poxidation and alcohols oxidation. In 2009, our group reported the first example of acid-catalyzed

reaction-controlled phase transfer catalytic system by preparing a series of new type ionic liquids (ILs) modified POM catalysts, in which the phase transfer process was controlled by the substrates in esterifications rather than H_2O_2.[11] Figure 6 presented the structure of these nonconventional heteropolyanion-based ILs (HPA-ILs: $[MIMPS]_3PW_{12}O_{40}$, $[PyPS]_3PW_{12}O_{40}$, and $[TEAPS]_3PW_{12}O_{40}$) tethered with propane sulfonate functionalized organic cations.[62] These hybrids had high melting points above 100 °C and were in solid state at room temperature due to the high electrostatic potential together with the extended hydrogen bonding networks between anions and cations. They were featured of excellent solubility in water or strong polar solvents but nonmiscibility with apolar esters. When these HPA-IL solid catalysts, such as
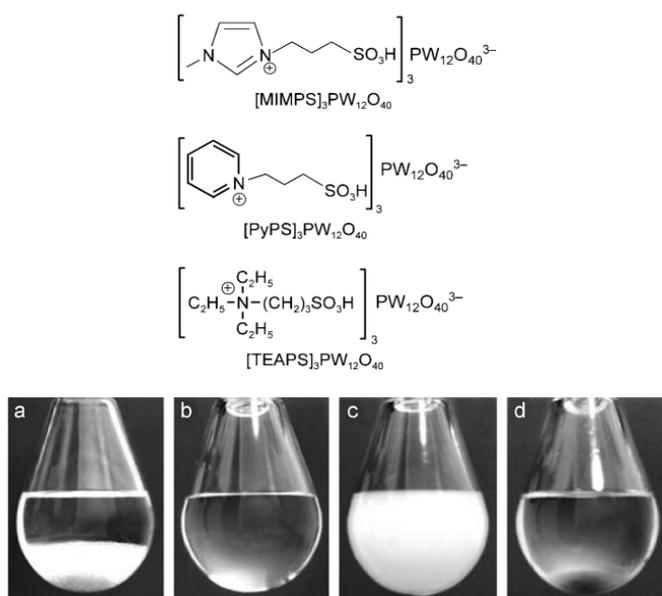
Figure 6 Upper: a series of novel heteropolyanion-based ILs. Bottom: photographs of the esterification of citric acid with *n*-butanol over $[MIMPS]_3PW_{12}O_{40}$. a) $[MIMPS]_3PW_{12}O_{40}$ (light brown solid at bottom), citric acid (white solid in the middle), and alcohol (liquid in the upper level) before mixing; b) homogeneous mixture during the reaction; c) heterogeneous mixture near completion of the reaction; d) at the end of the reaction; the catalyst has precipitated. Reprinted with permission from ref. 11. Copyright (2009) Wiley-VCH.

$[MIMPS]_3PW_{12}O_{40}$, were used for catalyzing esterication reactions, they could be dissolved completely in the medium to form a homogeneous mixture at the beginning of the reaction. In other words, with one of the reactants being polycarboxylic acid or polyol, they were dissolvable in one substrate (at reaction temperature in case of polycarboxylic acids, or at room temperature in in case of polyols). Thus, homogeneous catalysis happened at the reacting stage of the esterications. With the consumption of the polycarboxylic acids or polyols, the system became heterogeneous due to the insolvable property of these catalysts in the products, inducing a spontaneous self-separation of the catalyst (Figure 6). As a

result, these heteropolyanion-IL catalysts were used as "reaction-induced self-separation catalysts" in the esterication reactions. High yield of 95.4% and selectivity of 98% for tributyl citrate were obtained at 130 °C for 3 h. The catalysts could be facilely recovered and reused.

In our following works, we explored the design concept on the fabrication of various other IL-POM catalysts by combining modified IL-structured cations with heteropolyanions and investigated their performances in different phase transfer catalytic processes. In similar period of 2009, Leng et al. prepared a family of solid organic HPA salts by combining Keggin heteropolyanions with IL-cations functionalized by propane sulfonate (PS).[63] The obtained hybrid materials were used as PTCs in esterifications and could be easily recovered and reused without substantially changing the original structure of catalyst, demonstrated by a seven-run test. At the
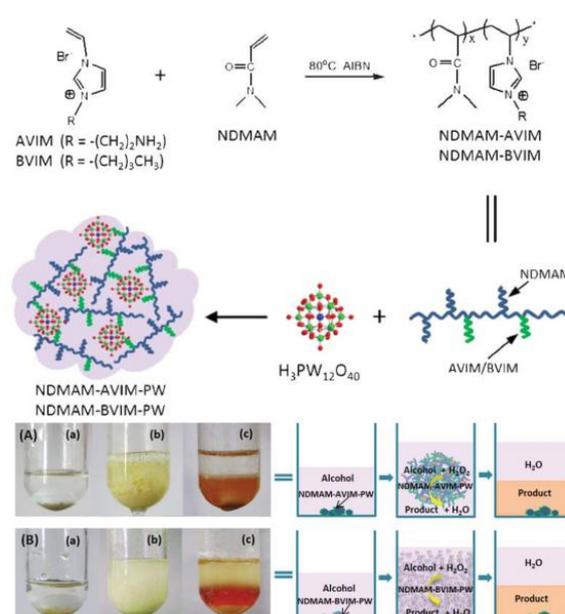
Figure 7 Upper: synthesis of the HPA-based polymeric hybrids. Bottom: photographs of the solvent-free oxidation of benzyl alcohol with H_2O_2 over (A) NDMAM-AVIM-PW and (B) NDMAM-BVIM-PW: (a) catalyst (light brown solid at bottom) and alcohol (liquid) before mixing; (b) during the reaction after adding H_2O_2; (c) at the end of the reaction. Taken from ref. 47 with permission from RSC Publications.

same time, Zhang et al. synthesized a new organic HPA salt by coupling SO_3H-functionalized triphenylphosphonium with phosphotungstic anion.[64] The resultant hybrid acted as a highly efficient catalyst for wide esterifications affording the target esters with quite steady reusability. Afterwards in 2012, Leng et al. reported the synthesis of heteropolyanion-based polymeric hybrids by ion-exchanging the task-specific designed ionic copolymers with Keggin heteropolyacids (Figure 7).[47] The hybrids were demonstrated to be highly efficient, conveniently recoverable and steadily reusable catalysts for the oxidation of

alcohols with H_2O_2. During the reaction, the catalyst presented a swelling behavior after the addition of H_2O_2. After reaction, the catalyst returned to its original powdery solid state at the bottom of the reactor, accompanying with the release of the product benzaldehyde from the aqueous upper phase to the oil lower layer, which allowed easy separation of both the solid catalyst and the insoluble product (Figure 7). The above special phase transfer procedure was probably induced and controlled by the reaction temperature and H_2O_2. In 2013, Zhao et al. reported the preparation and application of nitrile-tethered pyridinium polyoxometalate obtained by anion-exchange of the IL precursor [N-butyronitrile pyridine]Cl ([C3CNpy]Cl) with Keggin phosphovanadomolybdic acid $H_5PMo_{10}V_2O_{40}$ (PMoV2).[12] The influence of various IL-cations on the phase transfer catalytic performance was studied. The obtained hybrid [C3CNpy]4HPMoV2 gave rise to the first example of reaction-controlled phase-transfer hydroxylation of benzene with H_2O_2 (Figure 8), showing a very high yield to phenol of 31.4%. A considerable catalyst recovery rate of 87% was gained and a stable recycling activity was observed when a slight fresh catalyst was added.
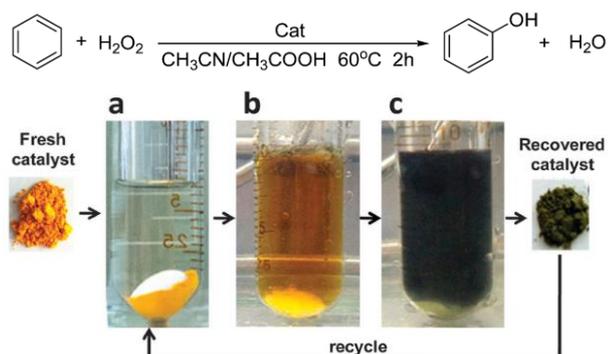
Figure 8 Photographs of [C3CNPy]4HPMoV2-catalyzed phase-transfer hydroxylation of benzene with H_2O_2; reaction conditions: catalyst 0.1 g, molar ratio of H_2O_2 to benzene 3:1, amount of the mixed solvent acetonitrile and acetic acid (volume ratio 1:1) 6 mL, 60 °C, 2 h. (a) reaction mixture without adding H_2O_2; (b) homogeneous solution after adding H_2O_2; (c) precipitation of the catalyst at the finish of the react ion; the white solid is the stirring bar. Taken from ref. 12 with permission from RSC Publications.

Since 2009, a series of IL-tethered POM-based PTCs were reported by other research groups. In 2009, Qiao et al. prepared two protic N-dodecylimidazolium peroxotungstate [HDIm]2[W2O11] and N-hexylimidazolium peroxotungstate [HHIm]2[W2O11] by the protonation of corresponding alkylimidazoles followed with pairing of the protic alkylimidazolium cations with [W2O11]2- anion (Figure 9).[28] The catalyst [HDIm]2[W2O11] was a room temperature liquid molten salt (ionic liquid) and could effectively catalyze the epoxidation of cyclooctene. This catalyst was regarded as a reaction-induced phase-separation catalyst, causing the switch of reaction system from tri-phase to emulsion, then to biphase, and finally to self-precipitating of the catalyst after the

reaction. In 2010, Li et al. synthesized a family of polyoxometalate-based ionic liquids by partial exchange of the protons of $H_3PW_{12}O_{40}$ with a PEG-2000 chain-functionalized alkylimidazolium chloride.[65] The catalyst showed high activity with excellent yields of esters in the esterification of various alcohols with acetic acid. During the reaction, an emulsion formed and could be conveniently broken by the addition of a weakly polar organic solvent, facilitating not only the catalytic reaction but also the separation of products. A direct transformation of benzaldehyde to methyl ester was also
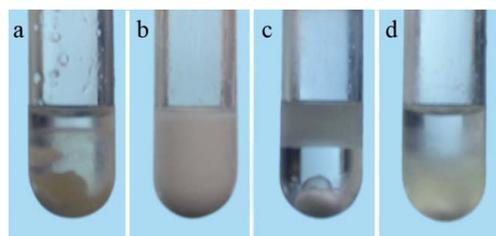
Figure 9 Photograph of the epoxidation of cyclooctene over the [HDIm]2[W2O11] catalyst in the mixed solvent of CH3OH-H2O (volumeratio=1:3). a) [HDIm]2[W2O11] (pale yellow viscous liquid at the bottom),mixed solvent of CH3OH-H2O (transparent liquid in the middle), cyclooctene (transparent liquid in the upper layer); b) emulsification of the system after reaction for 10 min; c) biphasic system was observed after reaction for 1 h with the catalyst dispersed in the substrate phase while the mixed solvent was transparent; d) at the end of the reaction, the pale yellow IL catalyst self-precipitated at the bottom of the flask. Taken from ref. 28 with permission from RSC Publications.

developed in the absence of any co-catalyst, presenting well substrates compatibility and recyclability. In 2012, Rafiee et al reported the synthesis of various polyoxometalate-based acid salts by combining Keggin anion with sulfonated ammonium, imidazolium and pyridinium cations.[38] Depending on the polarity of reaction mixture, these catalysts exhibited "self-separation" or heterogeneous performance in the synthesis of β-ketoenol ethers. The sulfonated pyridinium cation with $SiW_{12}O_{40}^{4-}$ anion ([PyPS]4SiW) showed the best activity and could be reused several times without significant loss of activity. In 2013, Zhuang et al. synthesized three hydrophobic Keggin-type heteropolyacid catalysts, [C3H3N2(CH3)(C2H4)]5PMo10V2O40 ([C2mim]PMoV), [C3H3N2(CH3)(C4H8)]5PMo10V2O40 ([C4mim]PMoV) and [C3H3N2(CH3)(C6H12)]5PMo10V2O40 ([C6mim]PMoV), by reacting molybdovanadophosphoric acid with imidazolium bromides.[66] These catalysts presented nearly 100% sulfur removal rate in the extractive catalytic oxidative desulfurization process using H_2O_2 as the oxidant and acetonitrile as co-solvent. The catalyst could be recycled six times with only a slight decrease in activity. In 2014, Han et al. prepared a series of IL-modified POM-based PTCs, PPS-TPA IL ([PPSH]xH3-xPW12O40; x=1.0-3.0), by incorporating varied amounts of tungstophosphoric acid (TPA) and pyridinium propyl sulfobetaine (PPS) zwitterionic

precursor.[67] They were exploited for homogeneous conversion of biomass such as acetalization of benzaldehyde with glycol. The catalyst system revealed self-separation characteristics. The $[PPSH]_2HPW_{12}O_{40}$ catalyst exhibited excellent durability and an optimal acetal yield over 85%, which can be attributed to their highly acidic nature and weak mass transport resistance. In 2014, Liu and co-workers reported a series of catalysts consisting of pyridinium propyl sulfobetaine (PPS), tungstophosphoric acid (TPA) and acetic acid (HOAc).[30] When tested in catalytic acetylation of glycerol (GL), these catalysts tended to segregate from glycerol acetate products to form distinct biphasic liquid layers spontaneously after the reaction, facilitating facile separation of products and recycling of catalyst (Figure 10). A complete GL conversion might be achieved with a superior glycerol triacetate (GTA) selectivity of 86-99%. In 2015, Zhou et al. reported the synthesis of $Mo_8O_{26}^{4-}$ based organic polyoxomolybdate salts and their application in olefin epoxidation using H_2O_2 as oxidant in CH_3CN.[14] With the formula $[Hmim]_4Mo_8O_{26}$ (Hmim=1-hexyl-3-methylimidazolium), $[Dhmim]_4Mo_8O_{26}$ (Dhmim=1,2-dimethyl-3-hexylimidazolium) and $[Hpy]_4Mo_8O_{26}·H_2O$ (Hpy=1-hexylpyridinium), these catalysts exhibited excellent catalytic performance, self-separating phenomenon, and good reusability for at least 10 runs without significant loss of activity.
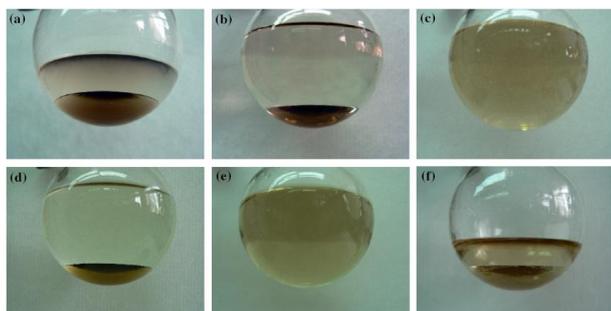
Figure 10 Snapshots of the homogeneous PPS-TPA-HOAc catalyst (a) before and (b) after introducing GL and HOAc reactants, (c) after thorough stirring at room temperature, (d)after acetylation reaction at high GL conversion while under continuous removal of water, (e) after initial acetylation reaction at low GL conversion, and (f) after the removalof excessive HOAc from mixture in (e). Reprinted with permission from ref. 30. Copyright (2014) Elsevier.

Very recently, more reaction-controlled POM-based PTCs were fabricated by employing cationic surfactant, oligomers or traditional quaternary ammonium salts. In 2014, Chen et al. reported the synthesis of dendritic phosphotungstate hybrids (dendri-PW hybrids) by incorporation of $PW_{12}O_{40}^{3-}$ into the polyamidoamine (PAMAM) matrix through partly protonating the amino groups of PAMAM dendrimer (Figure 11).[27] The dendritic PAMAM matrix not only finely tuned the redox properties of the PW anions, but also exerted a positive "dendrimer effect" on the enhancement of catalytic activity. The catalysts presented high conversion of alcohols in the selective oxidation of alcohols with H_2O_2 and could be reused

several times without loss of activity and selectivity. Besides, such matrix imparted the reaction-controlled phase-transfer function, differing from the dendritic POMs reported by Neumann's group,[68.69] the recovery of which required the concentration of the $CDCl_3$ layer under reduced pressure with the successive addition of pentane. In 2014, Ding and co-workers prepared a reaction-controlled silicotungstate-based phase-transfer catalyst $[(C_{18}H_{37})_2(CH_3)_2N]_3-[SiO_4H(WO_5)_3]$ for the oxidation of hydrocarbons.[33] The specificity of this catalyst
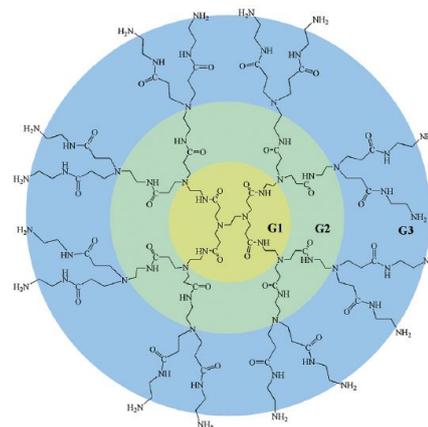
Figure 11 The structures of the PAMAM dendrimer (G1, G2 and G3). Taken from ref. 27 with permission from RSC Publications.

was the utilization of a heteropoly compound with silicon as heteroatom, differing from the previously reported reaction-controlled phase transfer catalysts always with phosphorus as heteroatom. The catalyst successfully catalyzed several oxidation reactions using H_2O_2 as oxidant and ethyl acetate as solvent, including 1) alkenes (such as linear terminal olefins, internal olefins, cyclic olefins and unactivated alkenes) to epoxides, 2) sulfides to sulfoxides and sulfones, 3) alcohols to carbonyl compounds. The usage of toxic solvents was ignored in the phase transfer catalytic process by this recyclable and environmentally benign catalyst. The epoxidation of cyclohexene was performed twenty times without obvious loss in activity. In 2014, Yu et al. prepared several organic salts of polyoxometalates, including $[π-C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$, $[π-C_5H_5NC_{12}H_{25}]_3[PW_4O_{16}]$, $[π-C_5H_5NC_{16}H_{33}]_3[PMo_4O_{16}]$, $[π-C_5H_5NC_{12}H_{25}]_3[PMo_4O_{16}]$ and $[π-C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$.[40] They were proved to be effective and recoverable phase-transfer catalysts for the oxidative desulfurization of simulated and real diesels. In 2015, Yahya et al. prepared the polyisobutylene (PIB) oligomer-bound polyoxometalates from the *in situ* self-assemble process by mixing commercial Keggin POMs and amine terminated PIB oligomer (Figure 12).[26] The catalysts were used as efficient and recyclable catalysts for environmentally benign biphasic oxidations by using H_2O_2 as oxidant. Desulfurization and alkene epoxidation reactions were found to be efficiently carried out in a heptane-water two-phase system. The reactions occurred through facile phase transfer of the peroxo POM intermediates into the

heptane phase that was facilitated by selective dissolving PIB oligomer (Figure 12).

$$(2)$$

6 (PIB$_{1000}$-CH$_2$CH$_2$NEt$_2$)

$$(3)$$

7 (PIB$_{1000}$-CH$_2$CH$_2$N(Et)$_2$CH$_3^+$I$^-$)
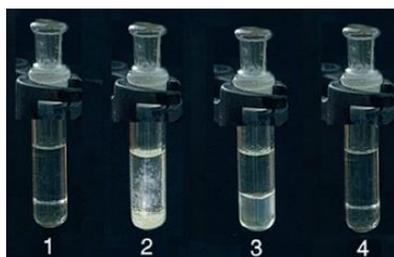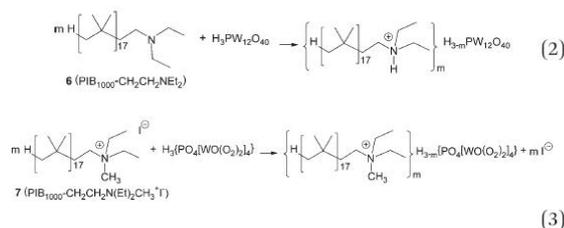
Figure 12. Upper: synthesis of the polyisobutylene (PIB) oligomer-bound polyoxometalates. Bottom: Catalyst recycling and phase behaviour in DBT oxidation inheptane-water two-phase system catalysed by PIB-PW (for better presentation, the amount of aqueous phase was increased five-fold): (1) initial reaction system with heptane phase (top) and aqueous H$_2$O$_2$phase (bottom); (2) the system after the first reaction run was complete, showing DBT sulfone (white precipitate); (3) the system after second extraction with acetonitrile-heptane phase (top) and acetonitrile phase(bottom); (4) the system ready for second run with fresh amounts of DBT and aqueous H$_2$O$_2$ added. Taken from ref. 26 with permission from RSC Publications.

2.4 Temperature-controlled phase transfer catalysis

The temperature-controlled POM-based PTCs were fabricated by designing temperature-sensitive POM catalysts that are dissolved or become emulsion in suitable medium at a high temperature and precipitated at room temperature (Figure 13). However, this type of POM catalyst is still rare and only several examples have been reported up to now.

The pioneer work was done In 2003 by Neumann and co-workers who synthesized the fluorous polyoxometalates, $(RFN^+)_{12}[WZnM_2(H_2O)_2(ZnW_9O_{34})_2]$, by using polyfluorinated quaternary ammonium cations, $[CF_3(CF_2)_7(CH_2)_3]_3CH_3N^+$ (RFN^+) as the countercation of polyoxometalate $[WZnM_2(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ (M = Mn(II), Zn(II)).[70] The obtained hybrid was freely soluble in perfluorohydrocarbons at room temperature. However, in other common solvents such as ethyl acetate and toluene, it was insoluble at room temperature but dissolves upon heating to 60-80 °C. Therefore, the above hybrid can be used as the thermal responsive catalyst in alcohol and alkenol oxidations, and alkene epoxidation with H$_2$O$_2$. Successively, Neumann and co-workers also studied other $[WZnM_2(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ based POM hybrids containing polymer-bound ammoniums. These

hybrids were active in the oxidation of 2-alkanols to 2-alkanones or oxidation of diphenylsulfide, though no thermal responsive phenomenon was reported.[71,72]
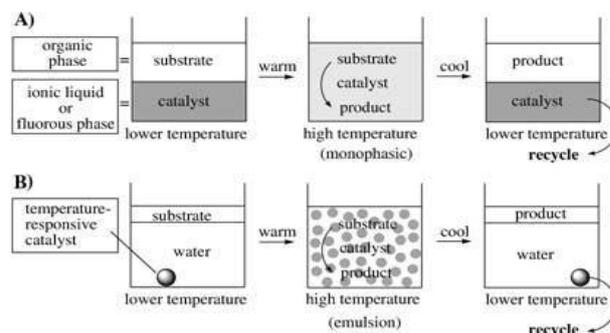
Figure 13 Simplified representation of thermomorphic catalysis. A) Use of a biphasic system comprising ionic liquids or fluorous solvents and an organic solvent. B) Use of a recyclable micellar-type reactionsystem. Reprinted with permission from ref. 10. Copyright (2005) Wiley-VCH.

In 2005, Hamamoto et al. developed a recyclable catalyst based on a POM-derived temperature-responsive material composed of phosphotungstic acid (H$_3$PW$_{12}$O$_{40}$) and poly(N-isopropylacrylamide) (PNIPAAm) polymer (Figure 14).[10] The catalyst was insoluble in most solvents at room temperature, but can form a stable emulsion in water at high temperatures. Besides, the catalyst was insoluble in nonpolar solvents (toluene or octane) and soluble in polar organic solvents (acetonitrile or tert-butyl alcohol) at high temperatures. It presented well catalytic activity in the oxidation of various primary and secondary alcohols with H$_2$O$_2$. After reaction, the catalyst precipitated on cooling and was cleanly separated from the reaction mixture after the addition of diethyl ether, thus could be easily recovered and reused. In 2007, Hamamoto et al. further applied the above catalyst in the oxidative cyclization with H$_2$O$_2$ to oxygen heterocycles.[73] The reaction occurred in water and presented thermo-regulated phase transfer phenomenon. In 2010, Zhao and co-worker presented two peroxopolyoxometalate-based room temperature ionic liquids (POM-RTIL) by pairing alkylimidazolium cation with the well-defined Venturello anion ($\{PO_4[WO(O_2)_2]_4\}^{3-}$).[74] They were well dissolved in the solvent of ethyl acetate during the epoxidation reaction of various olefins and could be self-separated from the reaction media at room temperature after the reaction, leading to easy separation of the products from the IL catalysts *via* simple decantation. Recycling tests indicated that these POM-RTIL catalysts were recyclable for five times without significant loss of activity. In 2011, Yan and co-workers prepared a series of HPA salts by using various acidic IL cations and heteropolyaions such as PW$_{12}$O$_{40}^{3-}$, SiW$_{12}$O$_{40}^{4-}$ and PMo$_{12}$O$_{40}^{3-}$.[39] Assessed in the transesterification of trimethylolpropane (TMP), these catalysts presented a self-separation performance when

cooled down to room temperature after reaction, benefiting easy recovery andsteady reuse during an eight-run recycling test. Among these hybrids, the pyridinium with $PW_{12}O_{40}^{3-}$ as the anion ($[PyBS]_3PW_{12}O_{40}$) showed the best catalytic performance for the transesterification of trimethylolpropane with various methyl esters.
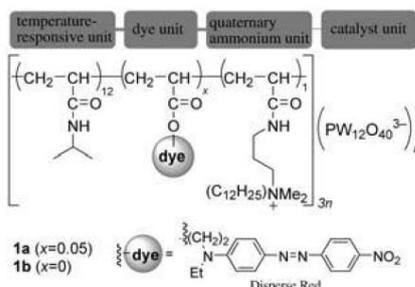
Figure 14 Design of thermomorphic polymer-supported $PW_{12}O_{40}^{3-}$. Reprinted with permission from ref. 10. Copyright (2005) Wiley-VCH.

Ding and co-workers also reported several temperature-responsive phase transfer catalytic systems by using POMs. In 2011, Ding et al. fabricated a facile and reusable catalytic system for alcohol oxidation with H_2O_2 over the catalyst $[(C_{18}H_{37})_2(CH_3)_2N]_{10}[SiW_9O_{34}]$.[75] It was prepared by combining dioctadecyldimethyl ammonium and trilacunarysilicotungstate anion of $[SiW_9O_{34}]^{10-}$. The catalyst exhibited temperature-responsive behavior in most organic solvents during the reaction, but formed an emulsion during the oxidation reaction in water. Several kinds of alcohols were efficiently oxidized in high yields. By cooling after the reaction, the catalyst was recovered from the mixture with the addition of diethyl ether, presenting a durable activity and selectivity after five cycles. In the same year, they reported another temperature-controlled phase transfer catalyst of $[(C_{18}H_{37})_2(CH_3)_2N]_7[PW_{11}O_{39}]$ that was used for the oxidation of pyridines and alcohols with H_2O_2 in 1,4-dioxane (Figure 15).[43] The catalyst was insoluble at room temperature, but dissolved with the elevation of reaction temperature, giving high yields of the corresponding heterocyclic N-oxides and ketones. After cooling down the reacted mixture, the catalyst precipitated gradually from the system itself and could be easily recovered and reused, giving no discernable loss in activity and selectivity after several reaction cycles. In 2013, Zhao et al. constructed a surfactant-encapsulated polyoxometalate $[(C_{18}H_{37})_2(CH_3)_2N]_8[HBW_{11}O_{39}]$ with the temperature-responsive property in the solvent of tert-butyl alcohol.[76] The catalyst was insoluble at room temperature, and became dissolvable with the elevation of reaction temperature. The emulsion state of the reaction mixture at room temperature was switched to clear solution by heating. When used in catalytic oxidation of pyridines with H_2O_2, the catalyst can be recovered and reused several times by controlling the reaction temperature.
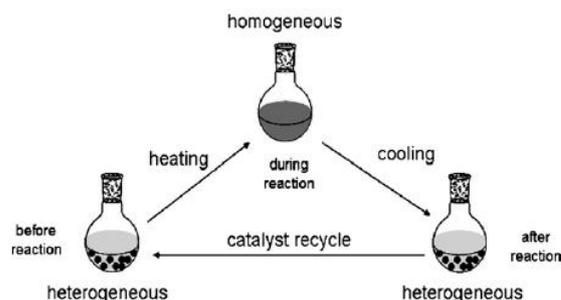
Figure 15 Representation of the temperature-controlled phase transfer catalytic system. Reprinted with permission from ref. 43. Copyright (2011) Elsevier.

In addition, there have been several studies examining the role of a covalent bond between a thermosensitive polymer and a POM on self-assembly and (photo)catalysis.[77-79] In 2012, Rieger et al. reported the synthesis of the POM-polymer hybrid $TBA_7[POM]$-poly(N,N-diethylacrylamide) (POM-PDEAAm) by grafting PDEAAm-NH_2 onto the activated Dawson acyl-POM, α_2-$[P_2W_{17}O_{61}SnCH_2CH_2C(=O)]^{6-}$.[77] The obtained material exhibited thermoresponsive properties with the lower critical solution temperature (LCST) of 38 °C. The result implies application potential in temperature-responsive phase transfer catalysis due to the reversible solubility/aggregation of the hybrid. In further work, the same group continued preparation of thermoresponsive POM-polymer hybrids containing PDEAAm and Dawson phosphotungstate.[78,79] The hybrids presented photocatalytic activity for the synthesis of silver nanoparticles under UV irradiation.[78] Even if no recycling test for the hybrids was examined, they showed a complementary aspect of the thermosensitive systems.

2.5 Photo-controlled phase transfer catalysis

For photo-controlled phase transfer catalytic system, only one example based on POM catalysts appeared so far, reported by Wu and co-worker in 2013.[13] The photo-responsive complex (Azo-SEP) with the formula of $[(AzoC_6)_2N]_9Na_3[Zn_5W_{19}O_{68}]$ was a surfactant-encapsulated polyoxometalate compound with photo-responsive azobenzene (Azo) units on the periphery (Figure 16). It was prepared through an ion-exchange reaction by mixing the aqueous solution of inorganic zinc-sandwich-structured POM cluster of $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ and the chloroform solution of organic surfactant (Azo-ended cationic surfactant). Reversible phase transfer of Azo-SEP complex was observed between toluene and H_2O/DMF (1:1 vol/vol) mixed solution upon UV and visible light irradiations, which was triggered by the photoisomerization-induced polarity change of Azo groups. The catalyst exhibited high activity and well reusability when used in photo-responsive phase transfer oxidation of sulfides to sulfones (Figure 16). By using the same concept, two other complexes were prepared by utilizing Azo-ended surfactants to encapsulate two different POMs, Keplerate-type $(NH_4)_{72}\{(Mo)$-

$Mo_5O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SO_4)\}_{30}(Mo_{132})$ and disk-like $K_{12.5}Na_{1.5}[NaP_5W_{30}O_{110}](P_5W_{30})$. These two complexes also presented similar reversible phase transfer upon UV and visible light irradiations and could be recycled through light-mediated reversible phase transfer in the catalytic process.
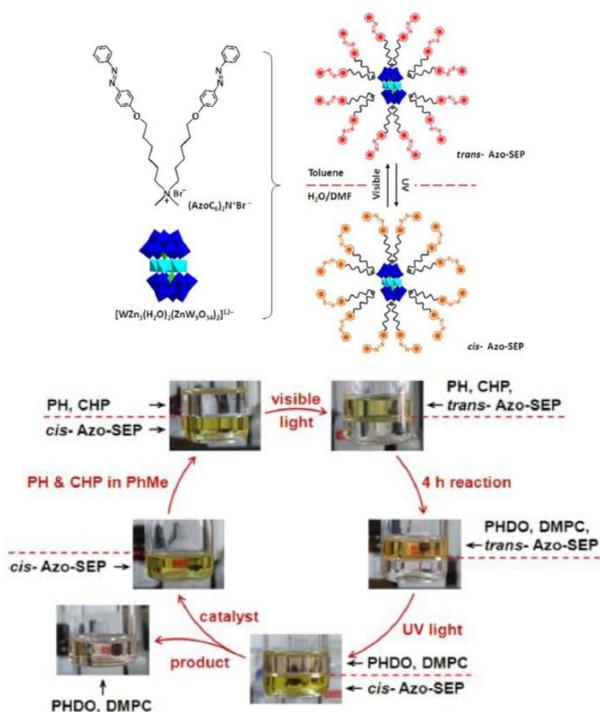
Figure 16 Upper: Chemical structures of cationic surfactant $(AzoC_6)_2N^+Br^-$ and a POM cluster and preparation of anAzo-SEP complex, as well as reversible phase transfer of the complex between toluene and H_2O/DMF mixed solution. Bottom: Schematic catalytic and phase-transfer recycle of photo responsive catalyst Azo-SEP, driven by alternate UV and visible light irradiations (reduced oxidant DMPC = dimethylphenylcarbinol). Reprinted with permission from ref. 13. Copyright (2013) American Chemical Society.

3. Conclusions and outlook

Various POM-based PTCs have been fabricated by modifying the POM anions with suitable organic cations. The versatile catalytic activity of POM anions enables the wide application of them in different reactions. These catalysts present well catalytic performances due to the homogeneous catalytic behavior during the reaction. Moreover, they can be facilely recovered and reused due to the special self-separation property. Thus, these catalysts combine the advantages of both homogeneous and heterogeneous catalysis, presenting promising potential in development of green and sustainable catalytic processes.

In current studies, there are mainly two types POM-based PTCs, i.e., reaction- and temperature-controlled phase transfer catalysts. Besides, there has appeared one example of photo-responsive phase transfer catalyst by using POM anions. Among them, the reaction-controlled PTCs are the most widely studied topic. These PTCs are mainly fabricated by Keggin-type POM anions, and their counter cations can be derived from quaternary ammonium salts, ILs, cationic surfactants and oligomers. IL-related anions with tunable molecular structures and functional groups become one promising versatile candidates for constructing multi-functional POM-based PTCs.

The POM-based PTCs turn out to be an attractive alternative for simultaneous preserving the high activity of a homogeneous catalyst and facilitating the recovery/reuse as a heterogeneous one, therefore providing a novel approach for efficient performance and easy recycling of POM-based catalysts. Though many efforts have been made, there still require further deep and extensive studies in this area, including the improvement of recovery rate of catalyst for minimize the leaching of active sites, especially in oxidation reactions by using H_2O_2; the insight of the phase transfer mechanism, task-specific designation of new efficient catalysts for wide applications, and involving computational chemistry for understanding catalytic mechanism and more accurate design of catalysts.

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