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Dendritic phosphotungstate hybrids efficiently catalyze selective oxidation of alcohols with H_2O_2

Yaju Chen,[a] Rong Tan,*[a] Weiguo Zheng,[a] Yaoyao Zhang, [a] Guangwu Zhao, [a] and Donghong Yin*[a,b]

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Keggin-type phosphotungstic acid (HPW) was incorporated into the polyamidoamine (PAMAM) matrix by partly protonating amino groups of PAMAM dendrimer. Characterization results suggested that the PAMAM dendrimer accommodated trivalent PW anions through ionic interactions and hydrogen bonds, resulting in novel dendritic phosphotungstate hybrids (dendri-PW hybrids). Derdritic PAMAM matrix as the countercation, not only fine-tunes the redox properties of the PW anions, but also plays a positive "dendrimer effect" on enhancing the catalytic activity of the hybrids. Higher conversion of alcohols was observed over the dendri-PW hybrids in the selective oxidation of alcohols with H_2O_2 as compared with that over the non-dendritic counterpart. Furthermore, the dendritic ammonium cation imparts reaction-controlled phase-transfer function to the dendri-PW hybrids. The catalysts precipitated from solvent with the consumption of H_2O_2, and could be reused for several times without loss of activity and selectivity.

Introduction

Polyoxometalates (POMs) are a large family of anionic metal−oxygen clusters of early transition metals.[1-4] They have drawn much attention in the fields of catalysis, since their redox potentials and acidities can be finely tuned by choosing the constituent elements and counteractions.[5,6] Recently, POMs, especially Keggin-type phosphotungstic acid ($H_3PW_{12}O_{40}$, HPW), have been widely used in the selective oxidation of alcohols with H_2O_2.[7-10] However, pure HPW utilized in their bulk form are often suffers from lower activity due to their very low surface area (<10 m^2. g^{-1}).[11,12] Furthermore, their recovery and reuse are also troublesome, because they can dissolve in reaction media.[13] As a result it is necessary to disperse the HPW onto the supports with large surface area. Although facile recovery, the heterogeneous HPW catalysts are plagued by mass-transfer limitations during reactions.[14,15] Therefore, development on highly active and reusable HPW catalysts for the selective oxidation of alcohols is desirably required.

Modification of HPW with organic units represents an effective approach to achieve HPW-based hybrid catalysts with improved catalytic activity and convenient catalyst reuse.[16-18] Different organic groups, such as ionic liquids,[19-21] and cationic surfactants,[22] have been employed to couple the PW anions through ionic bonds, giving organic-inorganic PW-based hybrid catalysts for selected reactions. The organic countercations can fine-tailor solubility and oxidizing capability of PW-based hybrids, optimizing the catalytic performance of catalysts.[23-25] For example, Hamamoto and coworkers developed a temperature responsive catalyst comprising poly(N-isopropylacrylamide) polymer cation and phosphotungstate anion ($PW_{12}O_{40}^{3-}$, PW).[26] The PW-based hybrid shows high activity in oxidation of various alcohols by H_2O_2 due to the formation of emulsion system, and could be easily precipitated from the reaction mixture upon cooling after the addition of diethyl ether. Xi et al. reported a quaternary ammonium cation coupled PW catalyst of $[\pi\text{-}C_5H_5N(C_{16}H_{33})_3]_3\{PO_4[WO_3]_4\}$.[27] The catalyst exhibited a unique reaction-controlled phase transfer behavior with the action of H_2O_2, showing excellent activity and reusability in the epoxidation of propylene with 30 *wt*.% H_2O_2.

Dendritic polyamidoamine (PAMAM), a highly branched macromolecule,[28-30] is an attractive organic modifier for POM. Some pioneering contributions to the dendritic POM hybrid are known in this emerging field. For example, Morgan and Cloninger prepared mannose functionalized PAMAM dendrimer supported Wells-Dawson type POM cluster $(Bu_4N)_5H_4P_2W_{15}V_3O_{62}$, which was efficient in the oxidation of alcohols with H_2O_2.[31] Chen and Cox fabricated a multilayer organic-inorganic nanocomposite by electrostatic assembly of ammonium PAMAM dendrimers with polyanionic Keggin-type $PMo_{12}O_{40}^{3-}$ species for electrocatalytic reduction of nitrite.[32] These interesting applications of PAMAM dendrimer in POM catalysis encouraged us to couple HPW with the PAMAM dendrimer to synthesize a dendri-PW hybrid for the oxidation.

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* [a] Institute of Fine Catalysis and Synthesis, Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education), Hunan Normal University, Changsha, Hunan, 410081, China;

[b] Technology Center, China Tobacco Hunan Industrial Corporation, NO. 426 Laodong Road, Changsha, Hunan, 410014, China.

Fax: +86-731-8872531; Tel: +86-731-8872576; E-mail: yiyangtanrong@126.com (R. Tan) or yindh@hunnu.edu.cn (D. Yin)

Multiple amino groups in PAMAM dendrimer can protonate with the acidic HPW, resulting in dendritic cation coupled PW hybrid. Different from the common organic cations, the dendritic countercation offers a local microenvironment for the PW anion, which may lead to the positive "dendritic effect" for the oxidation.[33,34] More importantly, mixed amino groups (both protonated and free amino groups) attached-organic cations are reported to fine-tune the redox properties of the PW anion, and further promote the activity and stability of PW-based catalyst.[14, 21,35]

With these points in mind, we decided to incorporate Keggin-type PW anion into the PAMAM dendrimer by partly protonating amine groups of the dendritic PAMAM with HPW to prepare PAMAM dendrimers hybridized phosphotungstate catalyst (**PW-PAMAM**). Dendritic PAMAM was expected to not only serve as a countercation to adjust the catalytic activity of the PW anion, but also achieve the positive "dendritic effect" for the selective oxidation of alcohols with H_2O_2. A portion of free amino groups remained in the PAMAM dendrimer to promote the redox property of PW species in cooperation with protonated amino groups. Moreover, we found that the dendritic PAMAM cation endows PW-based hybrids with a unique function: inverse dissolving-precipitating in water with the treatment of H_2O_2. Therefore, the catalyst could achieve the process of reaction-controlled phase-transfer catalysis in the selective oxidation of alcohols using aqueous H_2O_2 as terminal oxidant. Excellent efficiency was observed over the dendri-PW hybrids with the action of H_2O_2, which was significantly higher than that over non-dendritic counterpart. Activity switching was also repeatable even after five cycles, which typically realizes a homogeneous reaction coupled with biphasic separation in aqueous reactions. Thus, the problems associated with the separation of the catalysts and the mass transfer limitation in heterogeneous systems can be well resolved. In addition, the catalytic performance of the dendri-PW hybrids was also closely related to the generation of the dendritic scaffold.

Experimental

Materials and reagents

Keggin-type HPW was purchased from Sigma–Aldrich and used as received. Ethylenediamine and methyl acrylate were purchased from Alfa Aesar. Other commercially available chemicals were obtained from local suppliers. All of the solvents were purified by standard procedures before being used.[36] Other commercially available chemicals were laboratory grade reagents from local suppliers. PAMAM dendrimers with different generations (PAMAM-Gn (where n is the generation number, n=1, 2, 3)) (as shown in Chart 1) were prepared from procedures given in ref. 37.

Methods

Fourier transform infrared (FT-IR) spectra were obtained as potassium bromide pellets with a resolution of 4 cm^{-1} and 32 scans in the range 400–4000 cm^{-1} using an AVATAR 370 Thermo Nicolet spectrophotometer. The thermogravimetric and differential thermogravimetric (TG-DTG) curves were obtained on a NETZSCH STA 449C thermal analyzer. Samples were heated from room temperature up to 700 °C under flowing air using alumina sample holders. The sample weight was *ca.* 10 mg and the heating rate was 10 K/min. Elemental analyses of C, H and N were carried out on Vario EL III Elemental analyses made in Germany. ^1H NMR spectra of samples were recorded on a Varian-500 spectrometer with tetramethylsilane (TMS) as an internal standard. ^{31}P MAS NMR spectra were measured at room temperature on a Varian Infinitypuls-400 spectrometer using a Chemagnetic 4 mm double resonance probe. The Larmor resonance frequencies for 1H and 31P were 399.52 and 161.73 MHz, respectively. ^{31}P MAS NMR spectra with high power proton decoupling were recorded using a$\pi/2$ pulse length of 7.8 µs and a recycle delay of 30 s. The chemical shifts for the ^{31}P resonance were externally referred to $(NH_4)_2HPO_4$ (1.0 ppm). Thin layer chromatography (TLC) was conducted on glass plates coated with silica gel GF254. X-ray diffraction (XRD) patterns were recorded on a Philips X'PERT-Pro-MPD diffractometer using Cu-K_α radiation (λ= 1.542 Å) over the 2θ ranges of 5-60°. The content of tungsten in the samples was determined by inductively coupled plasma mass spectrometry, ICP-MS) on a Nexion 300X analyzer (Perkin-Elmer Corp.). The reaction products were analyzed by a gas chromatograph (Agilent Technologies 6890N, HP-624 capillary column, 30 m × 0.25 mm) with flame ionization detector (FID) using nitrogen as carrier gas. The products were identified by GC-MS using an HP5790 series mass selective detector.

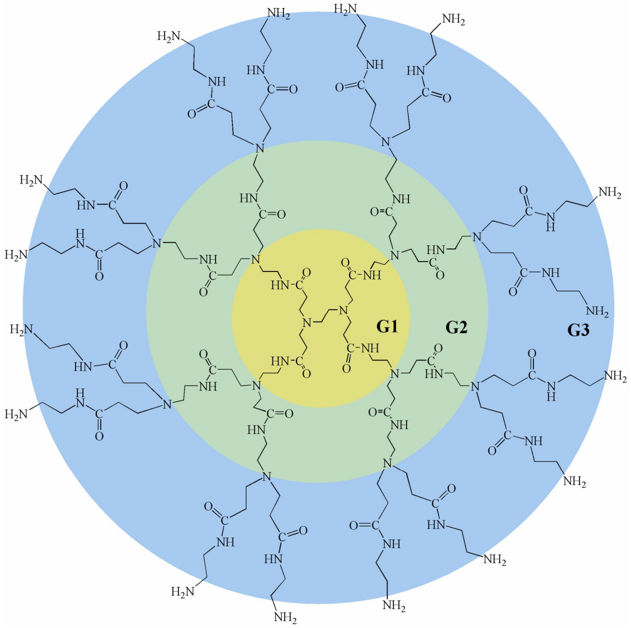

Chart 1 The structures of the PAMAM dendrimer (G1, G2 and G3).

Preparation of PW-PAMAM-Gn (where n is the generation number of PAMAM, n=1, 2, 3)

Synthesis of PW-PAMAM-G1: The preparation of **PW-PAMAM-G1** is outlined in Scheme 1. PAMAM-G1 (2.0 mmol) was mixed with Keggin-type HPW (3.0 mmol) in deionized water (20 ml) under room temperature. The mixture was stirred for 48 h. Upon filtration, the precipitate was washed with deionized water and ethanol, and then dried in vacuum overnight at 40 °C to afford grayish powder **PW-PAMAM-G1**. Elemental analyses found: C, 2.48; H, 1.25; N, 2.05%. PW content: 0.309 mmol/g

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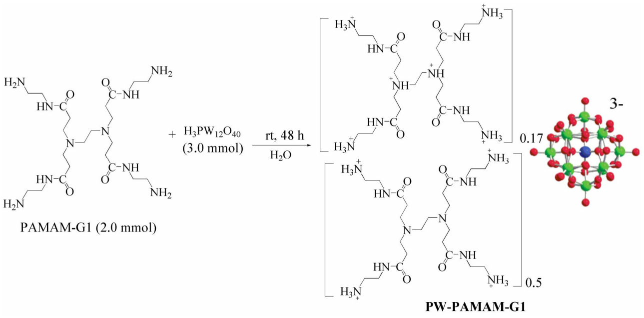
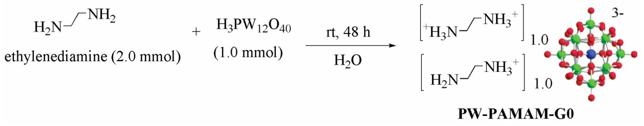
(calculated by the content of tungsten analyzed by ICP-MS), theoretical value: 0.318 mmol/g (all primary amine groups and tertiary amine groups totally protonated with HPW); FT-IR (KBr): γ_{max}/cm^{-1}: 3454, 3146, 3000, 2955, 2924, 2854, 1648, 1614, 1497, 1339, 1107, 1079, 1049, 979, 955, 895, 804, 596, 521.



Scheme 1 Synthesis of the **PW-PAMAM-G1**.

The dendri-PW hybrids of **PW-PAMAM-G2** and **PW-PAMAM-G3** with different PAMAM generations were also prepared according to the preparation procedure similar to that of **PW-PAMAM-G1**, except for the amount of HPW (6.0 mmol for G2 and 9.0 mmol for G3). The hybrids were also obtained as the grayish powder. **PW-PAMAM-G2**: Elemental analyses found: C, 8.21; H, 8.24; N, 4.41%. PW content: 0.297 mmol/g (calculated by the content of tungsten analyzed by ICP-MS), theoretical value: 0.314 mmol/g (all primary amine groups and tertiary amine groups totally protonated with HPW); FT-IR (KBr): γ_{max}/cm^{-1}: 3325, 3051, 2945, 1652, 1541, 1457, 1363, 1176, 1079, 1043, 946, 882, 801, 751, 596, 517. **PW-PAMAM-G3**: Elemental analyses found: C, 8.62; H, 2.14; N, 4.10%. PW content: 0.277 mmol/g (calculated by the content of tungsten analyzed by ICP-MS), theoretical value: 0.312 mmol/g (all primary amine groups and tertiary amine groups totally protonated with HPW); FT-IR (KBr): γ_{max}/cm^{-1}: 3361, 3080, 1653, 1544, 1457, 1394, 1367, 1250, 1189, 1080, 1044, 977, 950, 891, 805, 596, 516.

Synthesis of the PW-PAMAM-G0: For comparison, the non-dendritic counterpart of ethylenediamine-based PW hybrid was prepared by mixing Keggin-typed HPW with ethylenediamine in water with the molar ratio of ethylenediamine to HPW 2: 1, as shown in Scheme 2. Excess ethylenediamine resulted in the partial protonation of amino groups in ethylenediamine during the procedure. The obtained ethylenediamine-based PW hybrid was denoted as PW-PAMAM-G0. PW content: 0.330 mmol/g (calculated by the content of tungsten analyzed by ICP-MS), theoretical value: 0.336 mmol/g (all primary amine groups totally protonated with HPW); FT-IR (KBr): γ_{max}/cm^{-1}: 3490, 3149, 2963, 2932, 2871, 2647, 2508, 2348, 2316, 1603, 1489, 1471, 1384, 1162, 1079, 981, 888, 800, 595, 521.



Scheme 2 Synthesis of the PW-PAMAM-G0.

Synthesis of the PW/polyethyleneimine (PW/PEI) hybrid: Another dendrimer-free counterpart, in which polyethyleneimine (PEI) was used as the countercation, was also prepared by mixing Keggin-typed HPW (0.7 mmol) with excess PEI (Mw = 10000, 0.01 mmol) in water. The structure of the obtained PW/PEI hybrid is shown in Chart 3. PW content: 0.299 mmol/g (calculated by the content of tungsten analyzed by ICP-MS), theoretical value: 0.332 mmol/g (all amine groups totally protonated with HPW); FT-IR (KBr): γ_{max}/cm^{-1}: 3446, 3020, 2849, 1617, 1469, 1080, 1046, 981, 949, 891, 812, 733, 597, 519.

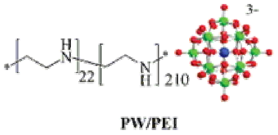


Chart 2 The structure of PW/PEI hybrid.

Catalyst testing

The catalyst of **PW-PAMAM-Gn** (1.5 mol‰, based on the PW loading) and alcohols (10 mmol) were added into a 50 ml flask. H_2O_2 (30 *wt.*%, 15 mmol) diluted with deionized H_2O (1.5 mL) was then added dropwise into the above mixture within 1 h. The resulting mixture was vigorously stirred at 100 ^oC. During the reaction, the system gradually changes from turbid to clear, and then becomes turbid again. The progress of the oxidation reaction was monitored on GC. After completion of the reaction, the precipitated catalysts were separated from the upper liquid phase by decantation. The catalysts were then washed with ethyl acetate, separated by decantation as described above, dried under vacuum overnight at room temperature for the recycle experiment. Ethyl acetate (3 × 10 mL) was used to extract the products from the reaction solution. The combined organic layers were dried with Na_2SO_4. Reaction products were analyzed by a gas chromatograph and further identified by GC-MS.

Results and discussion

Preparation of PW-PAMAM-Gn (n=1, 2, 3)

PAMAM dendrimer, a highly branched macromolecule possessing a multiple functional groups, has attracted much attention in the field of catalysis.[38] It can not only place catalytic sites in the dendritic scaffold through covalent/non-covalent method resulting in catalytically active macromolecules with facile reuse, but also provide unique "dendritic effect" beneficial to catalytic efficiency. The fascinating advantages encouraged us to incorporate the Keggin-typed HPW into the PAMAM dendrimers to achieve the efficient and recoverable dendri-PW hybrids for the selective oxidation of alcohols with H_2O_2. A strategy that we have designed here is partly protonating the multiple amino groups of PAMAM dendrimer with Keggin-type HPW. A portion of the amino groups remains free to fine-tune the redox property of W species in cooperation with the protonated amino groups, which in turn enhances the catalytic activity of the dendri-PW hybrids in selective oxidation reaction.

The dendri-PW hybrids were prepared simply by mixing Keggin-type HPW with excess PAMAM dendrimer in aqueous solution, where partial amine groups of the PAMAM dendrimer were protonated with Keggin-type HPW during the preparation procedure. The content of PW in the hybrids was measured in terms of tungsten percentage as obtained from ICP-MS results. It was found that the practical contents of PW in the dendri-PW hybrids were less than those theoretical calculations (all the

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primary amine groups and the tertiary amine groups totally protonated with HPW). We speculate that the protonation of PAMAM dendrimers first involves protonation of primary amine groups at the outer rim of the dendrimer, while the tertiary amine groups in the dendrimer interior protonate. The last group to protonate is a central tertiary amine due to the steric hindrance. Therefore, tertiary amine groups in the dendrimer interior and/or core should remain free. The PW active species should be primarily located at the periphery of the PAMAM dendrimer through ionic interactions. The featured structure will benefit for the accessibility of the active sites, and also enhance cooperative interaction between neighboring catalytic sites.

It is interesting to found that all the dendri-PW hybrids are insoluble in aqueous phase (Fig. 1A), but form water-soluble active species by the action of H_2O_2 (Fig. 1B), and when the H_2O_2 is used up, the catalyst precipitates again from aqueous phase (Fig. 1C). The unique solubility implies the reaction-controlled phase transfer function of the hybrids in the selective oxidation of alcohols with aqueous H_2O_2.

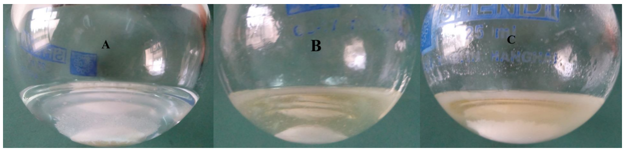

Fig. 1 Photographs of the fresh **PW-PAMAM-G1** (A), **PW-PAMAM-G1** treated with H_2O_2 (B) and **PW-PAMAM-G1** with the consumption of H_2O_2 (C) in reaction system.

Characterization of samples

Thermal analysis

The interaction of PW species with PAMAM dendrimer is characterized by means of TGA-DTG, as shown in Fig. 2. The sample of **PW-PAMAM-G1** hybrid shows four distinct steps of weight loss in the combined TG-DTG curves, when it is heated from room temperature to 700 °C under airflow (Fig. 2A). The first weight loss centers at 86 °C, which is due to removal of the surface-adsorbed water (a variable amount depending on the number of hydration waters in the sample). The second weight loss in the temperature range of 189–382 °C (*ca.* 6 *wt*.%) is logical to assign to the successive decomposition of PAMAM dendrimer unit in the **PW-PAMAM-G1**, since the dendritic PAMAM-G1 shows the similar major weight loss in the same temperature range (Fig. 2A vs C). The third weight loss appears at 516 °C, corresponding to the loss of constitutional water, which admittedly comprises Keggin-type species with oxygen vacancy.[39] Interestingly, this decomposition step is retarded as compared with that of the neat Keggin-type HPW (onset temperature shifts from 435 to 516 °C, Fig. 2A vs B), because of the interactions between PW species and dendritic PAMAM moiety in the **PW-PAMAM-G1** hybrid. Complete decomposition of the remaining organic cations (*ca.* 5 *wt*.%) occurs in the temperature range of 573–658 °C, and the non-removable residue was produced by the formation of constituent inorganic oxides in air at a high temperature.[14,40]

TGA analysis revealed that the PAMAM content of **PW-PAMAM-G1** is *ca.* 11 *wt*.% (0.2 $\mathrm{mmol.g^{-1}}$). The PW content can thus be estimated to be *ca.* 0.3 $\mathrm{mmol.g^{-1}}$ in the **PW-PAMAM-G1** hybrid, which is approximate to the content of PW moiety calculated from ICP-MS results (0.309 $\mathrm{mmol.g^{-1}}$). Furthermore, according to the TG data, we can draw that the dendritic PAMAM-G1 cation assembles with trivalent PW anion based on the molar ratios of 2: 3 in the **PW-PAMAM-G1** hybrid. Theoretically, 2 molar of dendritic PAMAM-G1 with 4 primary amine groups and 2 tertiary amine groups can couple with 4 molar of the trivalent PW anion. Therefore, a portion of amino groups remains free in the hybrid. As mentions, the primary amine groups at periphery are prior to being protonated, we can thus speculate that partial tertiary amine groups in the dendrimer interior are left free due to the steric hindrance. The structure of **PW-PAMAM-G1** hybrid is shown in Scheme 1. It is the mixed amino–attached dendritic cations that turn the **PW-PAMAM-G1** hybrid into a very active catalyst for this oxidation. The hybridizing behavior can be further confirmed by FT-IR spectroscopy.

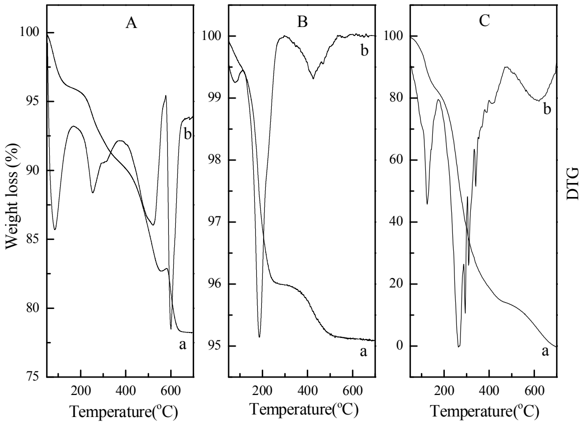

Fig. 2 TG–DTG curves of the **PW-PAMAM-G1** (A), Keggin-type HPW (B) and PAMAM-G1 dendrimer (C) ((a) thermogravimetric curves; (b) differential thermogravimetric curves).

FT-IR

Fig. 3 shows the FT-IR spectra of **PW-PAMAM-G1** hybrid, PAMAM-G1 and neat Keggin-type HPW. As shown in Fig. 3, PAMAM-G1 dendrimer shows the characteristic bands at 3279 and 3077 $\mathrm{cm^{-1}}$ corresponding to N-H vibrations of the primary amino groups (Fig. 3a).[41] But in case of the **PW-PAMAM-G1** hybrid, the bands disappear, along with the appearance of a new band assigned to primary ammonium salt at round 3000 $\mathrm{cm^{-1}}$ (Fig. 3a vs b).[42] The observation confirms that 4 primary amino groups in the PAMAM-G1 dendrimer are fully protonated with Keggin-type HPW, which consists with the speculation in TG analysis. Therefore, trivalent PW anions are mainly located at the periphery of PAMAM-G1 dendrimer through the ionic interaction. Only few of them are encapsulated within the cavities of dendrimer through the incorporation of internal tertiary amino groups. The ionic interaction can also be draw from the fact that four characteristic bands associated with the Keggin-type HPW[43] at around 1079 (P-O_a), 990 (W=O_d), 894 (W-O_b-W in corner shared octahedral) and 802 $\mathrm{cm^{-1}}$ (W-O_c-W in edge shared octahedral) show a slight shift in the FT-IR spectrum of **PW-PAMAM-G1** hybrid, although the characteristic bands still remain (Fig. 3b vs c). Especially, the characteristic band relating to asymmetric stretching vibration of W=O_d shifts from 990 to

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979 cm^{-1}, due to the ionic interaction in the hybrid.[14, 21, 35] Furthermore, the single P-O$_a$ vibration at 1080 cm^{-1} for the HPW is split into three bands at 1107, 1079 and 1049 cm^{-1} upon the hybridization (Fig. 3b vs c). As mentions, it is due to the formation of hydrogen bonds among the terminal oxygen atoms of PW anion and the amino groups in the dendritic scaffold.[21, 35] A strong and broad FT-IR band at around 3454 cm^{-1} attributable to N-H…N stretching vibrations was also observed for the **PW-PAMAM-G1** hybrid (Fig. 3c), indicating the presence of the hydrogen bonding networks between protonated and free amino groups.[21] Thus, the Keggin-type HPW was hybridized with PAMAM dendrimer through the ionic interaction, as well as the hydrogen bond networks.

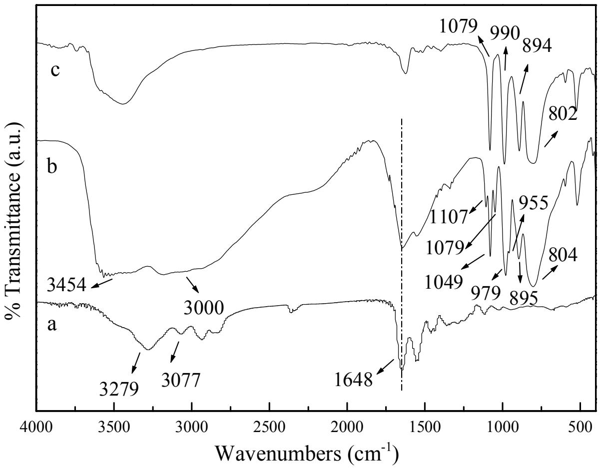

Fig. 3 FT-IR spectra of the PAMAM-G1 (a), **PW-PAMAM-G1** (b) and Keggin-type HPW (c).

After the hybridization, a new band at 955 cm^{-1}, assignable to the reduced W^{5+} species, appears as a branch of the band at 979 cm^{-1} for W=O$_d$ (Fig. 3b vs c), which suggests the co-existence of the low valent W^{5+} species together with the W^{6+} species in the hybrid.[35, 44] It indicates that the dendritic cation can tune the redox property of W species through the intramolecular charge transfer from the amino groups to PW species (W^{V} – O...AM). While, amide groups in the PAMAM dendrimer backbone does not take part in tuning the redox property of W species, since no change in the band at 1648 cm^{-1} corresponding to the amide groups is observed after forming the **PW-PAMAM-G1** hybrid (Fig. 3a vs. b). All the results encourage us to anticipate that PAMAM dendrimer hybridizes with Keggin-type PW anions through ionic bonds in connection with hydrogen bonds, and the dendrimer backbone remains intact during the hybridization.

XRD

XRD patterns were carried out to investigate the dispersion of the PW species in PAMAM dendrimer backbone. The wide-angle XRD patterns of the typical **PW-PAMAM-G1**, as well as the neat Keggin HPW, is shown in Fig. 4. A set of sharp Bragg peaks are obvious in the XRD pattern of HPW (Fig. 4a), which are characteristic of Keggin-type POMs. While, the characteristic Bragg reflections disappear in the XRD pattern of **PW-PAMAM-G1** hybrid despite the retainment of the Keggin structure of PW species during the hybridization (Fig. 4a vs b). It suggests that PW species successfully assembled with the **PAMAM** dendrimer through the ionic interaction, as well as hydrogen bonding, giving rise to a different semi-amorphous structure.[22,45] The XRD pattern for **PW-PAMAM-G1** hybrid illustrates only a new, broad Bragg reflection at 2θ = 7.9° (Fig. 4b), implying the existence of cavities among bulk cations and anions of this self-assembled hybrid.[46] The featured cavities may allow the permeating of substrates into the catalyst structure and enhance the accessibility of the active site in the bulk hybrid. The **PW-PAMAM-G1** hybrid can thus behave as a "pseudo-liquid" catalyst in the heterogeneous catalytic reaction.

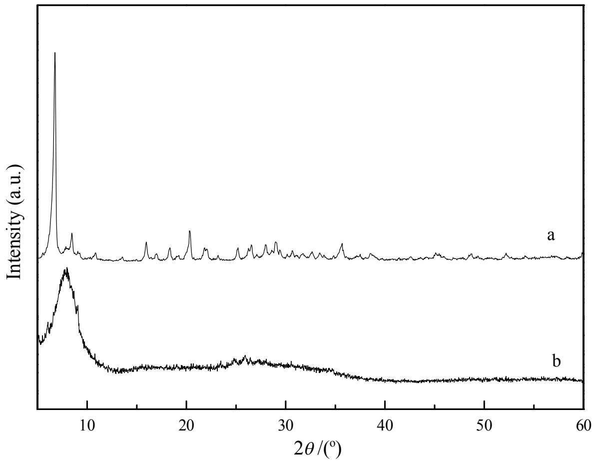

Fig. 4 Powder wide-angle X-ray diffraction patterns of the Keggin-type HPW (a) and **PW-PAMAM-G1** (b).

^{31}P MAS NMR

^{31}P MAS NMR is a powerful method to determine the local structures of the phosphorus in dendri-PW hybrids.[47-49] Fig. 5 depicts ^{31}P MAS NMR spectra of the typical **PW-PAMAM-G1**, and Keggin-type HPW for comparison. The ^{31}P MAS NMR spectra of hexahydrated HPW exhibits a single resonance at -15.5 ppm, which corresponds to the tetrahedral coordination of PO$_4$ in the Keggin unit (Fig. 5c).[14] Hybridization of HPW with PAMAM-G1 dendrimer leads to the formation of an additional line at -13.5 ppm (Fig. 5b), which can be attributed to the dehydrated PW anions.[14] The difference in ^{31}P MAS NMR spectra suggests the removal of structural water and three protons in the course of PW anchoring from aqueous solution on base functional groups of support. Similar results were discussed in the previous reports.[8, 14]

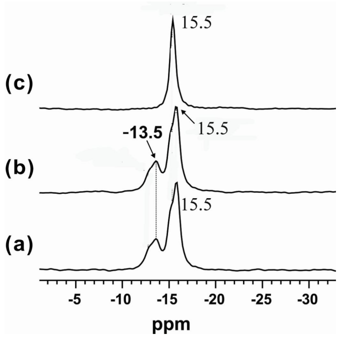

Fig. 5 ^{31}P MAS NMR spectra of the **PW-PAMAM-G1** (a), the recovered **PW-PAMAM-G1** (b) and Keggin-type HPW (c)

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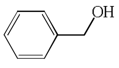
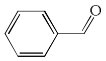
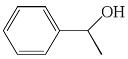
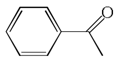
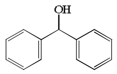
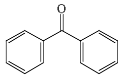
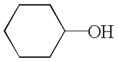
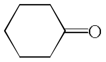
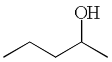
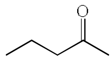
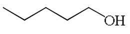
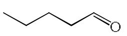
Catalytic performances

Although the dendri-PW hybrids are heterogeneous in aqueous phase, they can form water-soluble active species by the action of H_2O_2. Therefore, the reaction was performed under solvent-free condition with H_2O_2 as oxidant. The results of the selective oxidation of alcohols to corresponding aldehyde at 100 °C, using **PW-PAMAM-Gn** (n = 1, 2, 3) as catalysts and aqueous H_2O_2 as oxygen source, are summarized in Table 1. To demonstrate the positive "dendritic effect" originated from the dendrimer scaffold, the non-dendritic counterparts of ethylenediamine-based PW species (PW-PAMAM-G0) and PEI-based PW hybrid (PW/PEI) were prepared as the control catalysts by electrostatic coupling of anionic PW species with cationic ethylenediamine and PEI, respectively.

As expected, PW-PAMAM-G0 offered higher activity than neat Keggin-type HPW (Table 1, entry 3 vs. 1), due to the efficient tuning of redox property of W species by the mixed amino groups (NH_3^+ and NH_2-).[21,35] While, it was far less active than PW/PEI hybrid (Table 1, entry 3 vs. 4). Multiple active sites in the PW/PEI hybrid may result in cooperative interaction between neighboring catalytic sites, giving higher reactivity.[50] Enforcing cooperative interaction was observed when dendritic polymer was used as the countercations, since dendritic **PW-PAMAM-Gn** (n=1, 2, 3), especially, **PW-PAMAM-G1**, provided higher catalytic efficiency than PW/PEI hybrid (Table 1, entry 5 vs. 4). Using H_2O_2 as oxygen source, the novel **PW-PAMAM-G1** gave excellent conversion (94%) with high selectivity (96%) in the selective oxidation of benzyl alcohol to benzaldehyde within 6 h (Table 1, entry 5). Only 87% conversion of the benzyl alcohol with moderate selectivity (85%) was observed over PW/PEI under the identical reaction condition, although the water-solubility of the PW/PEI under the action of H_2O_2 (Table 1, entry 4). Notably, the PAMAM-G1 itself was inactive (Table 1, entry 2). The enhanced activity indicates that the dendritic scaffold plays a positive "dendrimer effect" in the reaction, and not simply acts as the countercation. In the case of the dendri-PW hybrid, dendritic PAMAM provides multiple and dense anchoring sites to the Keggin-type PW species, which controls and enforces the cooperative activation between neighboring catalytic sites. In addition, the bulkiness of dendritic cations may also account for the high activity of the dendri-PW hybrids, since the assembly of bulk dendritic cations with PW anions results in some cavities for the macrostructure,[46] through which substrates and oxidant can permeate into bulky hybrid unimpeded and access to the active W species. Apart from the enhanced activity of catalyst, free access of H_2O_2 also promotes the H_2O_2 efficiency. Near-stoichiometric molar of H_2O_2 was sufficient for the quantitative conversion of benzyl alcohol in the selective oxidation over **PW-PAMAM-G1**, giving excellent selectivity to benzaldehyde (Table 1, entry 5). While, excess amounts of H_2O_2 (H_2O_2/substrate molar ratio > 3) are often required for conventional POM-based catalysts, such as modified SBA-15 supported PW catalyst.[14] The enhancement of catalytic active and selectivity, as well as the high H_2O_2 efficiency, demonstrated the advantage of PAMAM dendrimer as the organic countercation.

Furthermore, various generations of PAMAM dendrimer (G1–G3) in **PW-PAMAM-Gn** were found to obviously affect the reactivity of corresponding hybrids in the selective oxidation. The activity of catalysts decreased with increasing generation number of the dendritic PAMAM scaffold. The first generation catalyst (**PW-PAMAM-G1**) showed the highest activity (94% conversion with 96% selectivity) in the selective oxidation of benzyl alcohol to benzaldehyde (Table 1, entry 5) under solvent-free condition. As the generation number of PAMAM dendrimer backbone increased from 1 to 2, and further increased to 3, the reactivity decreased accordingly (Table 1, entries 5–7). In the case of the third-generation species, only 86% conversion of benzyl alcohol was obtained in the oxidation. Selectivity to benzaldehyde was also decreased to 87% (Table 1, entry 7). This negative tendency is probably caused by the increased bulk around the catalytic center. Bulky cation increases distance between anionic PW and ammonium site in the hybrids, which thus attenuates the effect of mixed amino groups on tuning the redox property of active W species. Furthermore, increased bulkiness of the cation was reported to reduce the electrophilicity of the peroxopolyoxo species, which might be also result in lower reactivity of the corresponding hybrids.[34]

Table 1 Catalytic performance of various catalysts for the selective oxidation of alcohols [a]

Entry	Catalyst	Substrates	Products	Conv. [b] (%)	Sel. [c] (%)
1	neat HPW			65	69
2	PAMAM-G1 [d]			trace	/
3	PW-PAMAM-G0			80	86
4	PW/PEI			87	85
5	**PW-PAMAM-G1**			94	96
6	**PW-PAMAM-G2**			89	91
7	**PW-PAMAM-G3**			86	87
8	PW/PEI			80	>99
9	**PW-PAMAM-G1**			96	>99
10	PW/PEI			62	>99
11	**PW-PAMAM-G1**			80	>99
12	PW/PEI			53	>99
13	**PW-PAMAM-G1**			78	>99
14	PW/PEI			41	>99
15	**PW-PAMAM-G1**			50	>99
16	PW/PEI			11	75
17	**PW-PAMAM-G1**			13	90

[a] Catalyst (1.5 mol‰ of substrate, based on the PW loading), substrates (10 mmol), water (1.5 ml), H_2O_2 (30 *wt*.%, 15 mmol), 100 °C, 6 h. [b] Conversion was based on alcohols. [c] Selectivity was based on corresponding aldehydes or ketones. [d] PAMAM-G1 (7.74×10^{-3} g, 1.5 mol‰ of substrate), benzyl alcohol (10 mmol), water (1.5 ml), H_2O_2 (30 *wt*.%, 15 mmol), 100 °C, 6 h.

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The “cooperative effect” of catalytic sites along with the enhanced reactivity in the **PW-PAMAM-G1** is also noticeable in the case of the 1-phenylethanol, diphenylmethanol, cyclohexanol, 2-pentanol and 1-pentanol, as shown by conversions in Table 1 (Table 1, entry 5 vs. 4, entry 9 vs. 8, entry 11 vs. 10, entry 13 vs. 12, entry 15 vs. 14, entry 17 vs. 16). Conversions of the corresponding alcohols were found to be dependent on the nature of the substrates used in this work. Secondary alcohols were efficiently oxidized to the corresponding ketones under solvent-free conditions. 1-Phenylethanol achieved excellent conversion of 96% to benzophenone with 1.5 equivalents of H_2O_2 (Table 1, entry 9). Although secondary alcohols, relatively bulkier aromatic alcohol of 1,2-dihydronaphthalene underwent a slower oxidation over **PW-PAMAM-G1** (Table 1, entry 11). This is mainly due to the less accessibility of bulky substrate molecule to catalyst’s active sites. Aliphatic secondary alcohols, especially linear aliphatic alcohols, were less reactive than the aromatic secondary alcohols, giving moderate conversions (78% for cyclohexanol and 50% for 2-pentanol) to corresponding ketones (Table 1, entries 13 and 15). Aliphatic primary alcohols, such as 1-pentanol, are much difficult to oxidize under the solvent-free condition. Only 13% conversion of 1-pentanol was obtained with 1.5-fold molar excess of H_2O_2 (Table 1, entry 17).

Reusability

Apart from the positive cooperative effect for enhanced catalysis, another salient feature of the dendri-PW hybrids in reaction was the inverse dissolving-precipitating in water with the treatment of H_2O_2. When the H_2O_2 is used up, the catalysts precipitate quantitatively from the reaction system, as shown in Fig. 1C. The recovered hybrids are used for subsequent catalytic runs without further activation. Fig. 6 shows the results of the recovery and reusability of these dendri-PW hybrids. As expected, the recovered **PW-PAMAM-Gn** catalysts could be reused several times with no appreciable decrease in conversions and selectivity. The retention of catalytic efficiency suggests that although **PW-PAMAM-Gn** hybrids form water-soluble active species with the action of H_2O_2, they are reusable for the oxidation reaction.

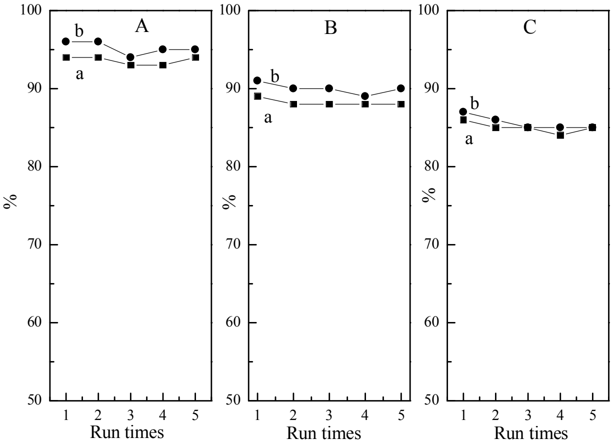

Fig. 6 The reuse of **PW-PAMAM-G1** (A), **PW-PAMAM-G2** (B) and **PW-PAMAM-G3** (C) in the selective oxidation of benzyl alcohol with H_2O_2 as oxidant (a: conversion; b: selectivity).

FT-IR spectroscopy technique was used to monitor the transformation of PW species with the treated with H_2O_2. **PW-PAMAM-G1** hybrid was employed as the typical catalyst for the investigation. FT-IR spectra of the fresh **PW-PAMAM-G1**, **PW-PAMAM-G1** treated with H_2O_2, and the recovered hybrid, are shown in Fig. 7. The fresh **PW-PAMAM-G1** displays the characteristic bands associated with the Keggin-type PW anions (Fig. 7a). Treatment with H_2O_2 results in the gradual disappearance of bands for W-O$_b$-W in corner shared octahedral (at 895 cm^{-1}) and W-O$_c$-W in edge shared octahedral (804 cm^{-1}) (Fig. 7b and c vs a). The distinguishing change suggests the degradation of intramolecular W-O-W of $[PW_{12}O_{40}]^{3-}$ into peroxobridged $[PW_4O_8(O_2)_8]^{3-}$ species by the reaction with H_2O_2. The resulted $[PW_4O_8(O_2)_8]^{3-}$ was water-soluble, and acted as the real active species for catalyzing alcohol oxidation. When the H_2O_2 was used up, the two characteristic bands at 895 and 804 cm^{-1} reappear (Fig. 7d), suggesting the regeneration of W-O$_b$-W and W-O$_c$-W bonds. The observation gives a strong evidence that soluble $[PW_4O_8(O_2)_8]^{3-}$ species transforms to the insoluble Keggin-type $[PW_{12}O_{40}]^{3-}$ species again after the reaction. We thus proposed that $[PW_4O_8(O_2)_8]^{3-}$ species and $[PW_{12}O_{40}]^{3-}$ species could be transformed to each other under the reaction condition, and most of $[PW_4O_8(O_2)_8]^{3-}$ species was transformed to $[PW_{12}O_{40}]^{3-}$ species after the reaction. Similar transformation has been reported by Zhang *et al*.[8]

The recovered catalyst from the reacted mixture gives the multiple FT-IR bands similar to the fresh one, verifying a rather durable catalyst structure that accounts for the steady reuse (Fig. 7a vs d). More evidence of the stability of the **PW-PAMAM-G1** catalyst was provided by the ^{31}P MAS NMR spectra of the **PW-PAMAM-G1**hybrid with fresh and reused for five times (Fig. 5a vs. b). No significant changes of the catalyst took place even after reuse for five times. Elemental analyses of the recovered **PW-PAMAM-G1** hybrid gave the content of C, H and N elements almost identical to those of the fresh one (recovered hybrid: C, 2.49; H, 1.26; N, 2.03%; fresh hybrid: C, 2.48; H, 1.25; N, 2.05%). Furthermore, negligible amount of soluble active species could be detected in the filtrate in terms of tungsten percentage according to ICP-MS analysis. The observations demonstrate the prefect stability of the **PW-PAMAM-Gn** catalysts in the H_2O_2 mediated-oxidation system without degradation and leaching.

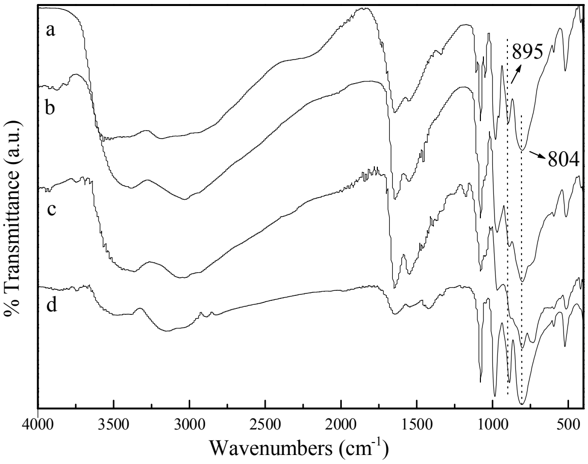

Fig. 7 FT-IR spectra of fresh **PW-PAMAM-G1** hybrid (a), the hybrid treated with H_2O_2 for 10 min (b), the hybrid treated with H_2O_2 for 30 min (c) and the recovered **PW-PAMAM-G1** hybrid (d).

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Conclusions

Keggin-type trianionic PW has been successfully hybridized with the ammonium PAMAM dendrimers through ionic interaction, as well as hydrogen bonds. The obtained dendri-PW hybrids, especially the first-generation catalyst, benefit from the positive “dendrimer effect”, exhibiting the excellent features of friendly environment, high efficiency and facile reuse in the selective oxidation of alcohols using aqueous H_2O_2 as terminal oxidant.

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