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A reusable catalytic system for sulfide oxidation and epoxidation of allylic alcohols in water catalyzed by poly(dimethyl diallyl) ammonium/polyoxometalate

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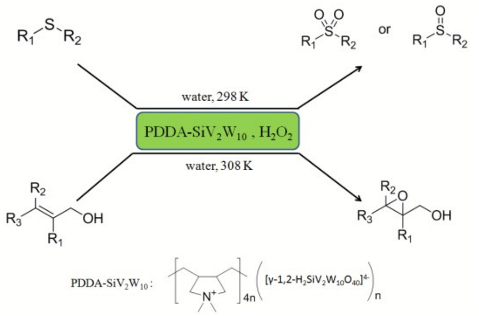
Wei Zhao*, Chunxia Yang, Zhiguo Cheng, Zhenghui Zhang

An effective catalyst based on polyoxometalate and polymer has been developed for oxidation of sulfides and allylic alcohols under mild conditions in water. The synthetic procedure of catalyst and the separate of the products are convenient, and the system is green and reusable.

Oxidative transformations of organic compounds are important in industry and synthetic chemistry [1]. From environmental and economical viewpoints, the stoichiometric procedures using classical toxic waste-producing oxidants are undesirable and replaced by environmentally benign oxidants with catalyst such as hydrogen peroxide and molecular oxygen, where their byproduct is water. Polyoxometalates (POMs) with well-defined inorganic transition-metal oxide clusters are commonly used in catalysis, medicine, imaging, sensing, and multifunctional materials [2]. POMs, as effective catalysts for oxidation reactions with hydrogen peroxide have drawn wide attention in the past years, such as alcohol oxidation, pyridine N-oxidation and alkane oxidation [3]. To solve the problem of catalyst reusability, several heterogeneous catalysts based on POMs have been designed and used in catalytic oxidations with hydrogen peroxide [4]. Although the catalysts could be recovered and reused, the poisonous organic solvents were necessary in these systems to keep the catalytic activity. From the stand points of green sustainable chemistry, oxidations of hydrophobic organic compounds that take place in nontoxic solvent have been received a great deal of attention. If the insoluble organic substrates could be oxidized with hydrogen peroxide in water with efficient catalysts, that will be more suitable for green industrial goals. It is a major challenge until now to accomplish the oxidations of organic compounds in aqueous media catalyzed by polyoxometalates with hydrogen peroxide.



Scheme 1 Oxidation of sulfides and allylic alcohols catalyzed by PDDA-SiV$_2$W$_{10}$ in water

The oxidation of sulfides to sulfoxides and sulfones is a pivotal reaction because its use in chemical industry, medical chemistry and biology [5]. Moreover, as the better alternative way compared with traditional hydrodesulfurization process, oxidative desulfurization to yield sulfoxides or sulfones, has aroused attention because of high desulfurization efficiency [6]. In the other hand, the oxidation of olefins to epoxides is a most valuable reaction in the chemical industry as well as in the laboratory because epoxides, with their reactive oxirane groups, are useful intermediates and precursors in various synthetic organic chemistry [7]. Many systems have been developed using polyoxometalates as catalysts for oxidation of sulfides and olefins [8]. However, efficient catalytic systems using polyoxometalates in green solvents with hydrogen peroxides are still rarely developed [9].

Poly (diallyldimethylammonium chloride) (PDDA), a linear positively charged polymer with green and stable property, has been used widely in industrial applications and material science [10]. However, the report of PDDA used in catalysis was less. Herein we report a simple, efficient, and green catalytic system for oxidation of organic compounds catalyzed by a composite catalyst based on PDDA and polyoxometalate. The more charge cation and strong water solubility of PDDA can be designed into a hybrid catalyst used in water during reaction. A polyoxovanadometalate of [γ-1,2-H$_2$SiV$_2$W$_{10}$O$_{40}$]$^{4-}$ is chosen to combined with PDDA to synthesize the catalyst, which is active

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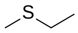
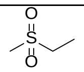
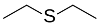
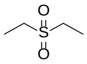
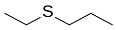
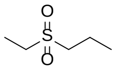
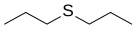
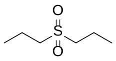
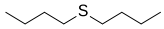
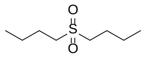
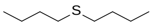
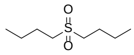
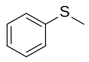
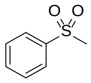
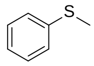
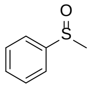
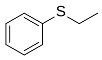
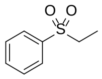
College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang 473061, China. Tel.: +86-377-63525056; Fax: +86-377-63525055. E-mail addresses: zhaowei1231@163.com

† Electronic Supplementary Information (ESI) available: General experimental information, characterization of catalyst, data of the products. See DOI: 10.1039/x0xx00000x

Table 1 Oxidation of sulfides in water using H_2O_2 catalyzed by PDDA-SiV_2W_{10} [a]

Entry	Substrate	Product	Time (h)	Yield (%) [b]
1			2	99
2			2	99
3			3	99
4			3	99
5			8	99
6[c]			8	<1
7			3	99
8[d]			5	90[e]
9			3	99

[a] Reaction conditions: catalyst (50 mg), substrate (2 mmol), H_2O_2 (30% aq., 10 mmol) and H_2O (2 mL) at 298 K. [b] Yields were determined by gas chromatography using an internal standard technique and are based on sulfides. The products were identified by GC-MS. [c] Blank experiment. The reaction was carried out without catalyst. [d] Reaction conditions: catalyst (50 mg), substrate (2 mmol), H_2O_2 (30% aq., 2 mmol) and H_2O (2 mL) at 298 K. [e] Sulfoxide (91% selectivity) and sulfone (9% selectivity) were formed.

for oxidations with hydrogen peroxide in mixed organic solvent of acetonitrile/tert-butyl alcohol [4b, 11]. The polymer surfactant and inorganic cores are easily combined together through electrostatic interaction (denoted as PDDA-SiV_2W_{10}). The hybrid catalyst is used herein to catalyze the oxidation of organic compounds in water with hydrogen peroxide. The catalyst shows high activity and interesting selectivity for the oxidation of sulfides and allylic alcohols in water under mild reaction conditions (see Scheme 1). In addition, the separation of product from catalytic system is very easy and the catalytic system is recyclable.

Since the solubility behavior in water of polymer cation of the catalyst, PDDA-SiV_2W_{10} shows high dispersibility in aqueous media. An emulsion was obtained in aqueous solution based on PDDA-SiV_2W_{10} including organic substrates and hydrogen peroxide. Hydrophobic organic compounds could be oxidized in this aqueous catalytic system under mild conditions.

Initially, oxidation of sulfides were detected using PDDA-SiV_2W_{10} in water with hydrogen peroxide at room temperature. Table 1 summarizes the results of catalytic oxidation of different sulfides in this aqueous system. Various kinds of sulfides were oxidized to the corresponding sulfones with 99% selectivity, including ethyl methyl sulfides, diethyl sulfides, ethyl propyl sulfides, dipropyl sulfides and dibutyl sulfides (Table 1, entries 1-5). The oxidation of dibutyl sulfides did not proceed in the absence of the catalyst under the same reaction conditions (Table 1, entry 6). Some aryl sulfides could be also converted into the corresponding sulfones in excellent yields (Table 1, entries 7 and 9). Interestingly, the present catalyst with 1.0 equivalent of hydrogen peroxide could also catalyze methyl phenyl sulfide to the corresponding sulfoxide in high selectivity (91%) along with formation of the corresponding sulfone (9% selectivity). Both aryl and alkyl sulfides could be converted into the corresponding sulfoxides or sulfones in high yields. We can see that the present catalytic system could successfully catalyze the reaction of organic substrates in aqueous solution.

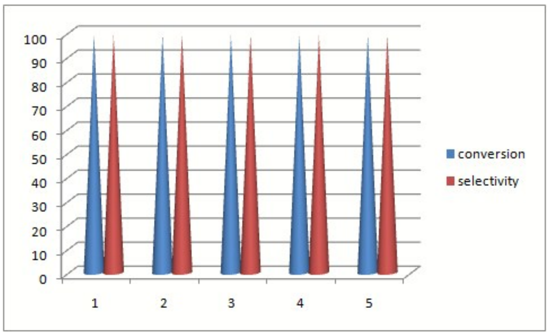
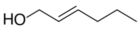
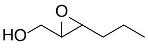
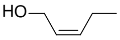
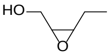
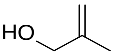
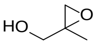
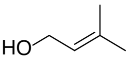
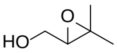
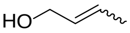
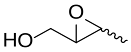
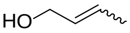
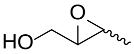
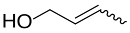
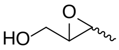
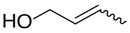
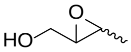


Figure 1 Recycling of the catalytic system for oxidation of methyl phenyl sulfide to the corresponding sulfone

The catalyst assembled with PDDA and polyoxometalate could be recovered and reused in the aqueous system. The cation of polymer plays an important role in the recycling of the catalyst. An emulsion was formed when the catalyst dispersed in aqueous solution. During reaction, the active emulsion catalyzed the oxidation of sulfides with hydrogen peroxide at room temperature. After reaction, the organic products were easily separated from the aqueous phase by extraction with ethyl acetate. The catalyst was still remained in the aqueous solution as a stable emulsion after extraction, and the aqueous phase could be used for the next run. The reuse performances of PDDA-SiV_2W_{10} in the oxidation of methyl phenyl sulfide are shown in Figure 1. After five consecutive reuses, there was no obvious loss of initial catalytic activity. The yield of sulfone obtained with the recovered catalyst was the same as that of the first reaction, indicating that catalyst is a reusable and robust catalyst in the oxidation system.

The present PDDA-SiV_2W_{10} catalytic system was also applied to the epoxidation of various kinds of allylic alcohols using only one equivalent of hydrogen peroxide in water, as shown in Table 2. Trans-2-hexen-1-ol, cis-2-penten-1-ol and crotyl alcohol were oxidized to the corresponding epoxides in high yields under mild conditions (Table 2, entries 1, 2 and 5). The active substrate of 3-methyl-2-buten-1-ol was oxidized to the corresponding epoxide during 1 hour at room temperature (Table 2, entry 4). However, the poor reactivity was obtained during the oxidation of 2-methyl-2-propen-1-ol (Table 2, entry 3). The reason of the catalytic results may due to the different electron donating structures of the substrates. The control experiment was also carried out to reveal that the oxidation of crotyl alcohol was hardly processed without catalyst (Table 2, entry 6). The reuse of the catalyst for epoxidation of crotyl alcohol is also shown in the Table (entries 5, 7 and 8). After three consecutive reused, there was no significant loss of initial catalytic activity.

Table 2 Epoxidation of various allylic alcohols with H_2O_2 in water catalyzed by PDDA-SiV_2W_{10} [a]

Entry	Substrate	Product	Time (h)	Yield (%) [b]
1			7	80
2			6	85
3			6	38
4[c]			1	79
5[d]			5	88
6[d,e]			5	0
7[d,f]			5	87
8[d,g]			5	88

[a] Reaction conditions: catalyst (50 mg), substrate (5 mmol), H_2O_2 (30% aq., 5 mmol) and H_2O (1 mL) at 308 K. [b] Yields were determined by gas chromatography using an internal standard technique and are based on substrates. The products were identified by GC-MS. [c] Reaction conditions: catalyst (50 mg), substrate (5 mmol), H_2O_2 (30% aq., 5 mmol) and H_2O (0.5 mL) at 298 K. [d] cis- and trans-mixture. [e] Blank experiment. The reaction was carried out without catalyst. [f] Reuse experiment of cycle 1. [g] Reuse experiment of cycle 2.

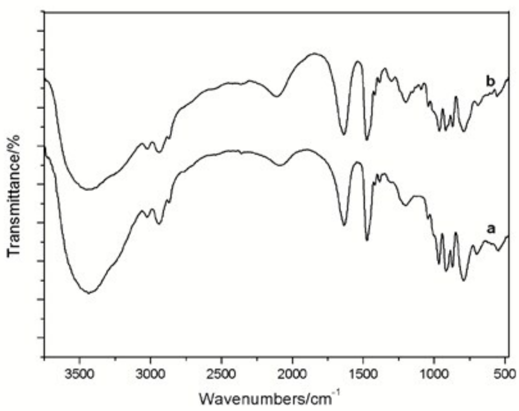


Figure 2 IR spectra of the catalyst before and after reaction: (a) the fresh catalyst; (b) the used catalyst

The fresh catalyst of PDDA-SiV_2W_{10} and the used catalyst were characterized with FT-IR spectra (Figure 2). The IR spectrum of PDDA-SiV_2W_{10} exhibited peaks at 1041, 967, 918, 871, 794, 702, 544 and 403 cm^{-1}, which is attributed to the polyoxometalate anion of $[\gamma\text{-}1,2\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$ [12]. Comparing the IR spectrum of the used catalyst with that of the fresh catalyst, the characteristic peaks were still existed and no fresh peaks appeared. There was no discernable difference between the IR spectra of the fresh catalyst and the used one, indicating that the structure of the catalyst was stable during the reaction in this aqueous system. Except for IR spectra, the catalyst was also detected by other characterizations, including XRD, TEM, SEM, BET, and so on (shown in Supporting Information). We can see that the particle size of catalyst range from 500-600 nm. Although the surface area of the obtained catalyst is not abundant, it did not affect the catalytic activity during reaction, which could be attributed to the particular aqueous emulsion based on PDDA-SiV_2W_{10}. In addition, the possible reaction mechanism of the catalytic system was also proposed referring to previous report [11c], which was also shown in Supporting Information. The anion of the catalyst ($[\gamma\text{-}1,2\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$) reacts with hydrogen peroxide to form finally the active vanadium oxygen species, which plays an important role in the oxidation of sulfides and allylic alcohols.

Conclusions

In this work, a peculiar catalyst combined by polymer and polyoxometalate (PDDA-SiV_2W_{10}) was synthesized and used in water for oxidation of sulfides and allylic alcohols under mild conditions. The catalytic system has the following advantages: (1) the synthesized method of catalyst is simple, and the desired material is safe and inexpensive; (2) the oxidation reactions are successfully carried out in water under mild conditions, the catalytic system is environmentally benign; (3) the organic products can be separated easily from aqueous system after reaction; (4) the catalytic system can be used several times with retention of the catalytic performance. So, the catalytic method described in this work possesses high practicability for green chemistry.

Acknowledgements

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An effective catalyst based on polyoxometalate and polymer has been developed for oxidation of sulfides and allylic alcohols under mild conditions in water. The synthetic procedure of catalyst and the separate of the products are convenient, and the system is reusable.