



Heterogenous Viologen Catalysts for Metal-free and Selective Oxidations

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Complete List of Authors:	Hou, Shengtai; Shanghai Jiao Tong University Chen, Nanqing; University of Tennessee, Department of Chemistry Zhang, Pengfei; Shanghai Jiao Tong University, Department of Chemical Engineering; Oak Ridge National Laboratory, Dai, Sheng; Oak Ridge National Laboratory,



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Heterogenous Viologen Catalysts for Metal-free and Selective Oxidations

Shengtai Hou,^a Nanqing Chen,^b Pengfei Zhang^{a, b,*} and Sheng Dai^{b, c*}Received 00th January 20xx,
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Metal-free oxidation, a green chemistry process has drawn more attention from catalysis community. However, most oxidation processes are complete by homogeneous metal-free catalysts, while heterogeneous metal-free materials have been developed with limited successes. In this work, polymerized ionic networks (PINs) with N, N'-dialkyl-4,4'-bipyridinium units as heterogeneous viologen type of catalysts exhibit high efficiency in oxidizing aromatic sulfide/alcohol to sulfoxide/aldehyde, respectively (Conv.: >90%, Sel.: >95%). The catalytic performance of PINs originates from the electron-accepting ability of viologen unit, which can reduce H₂O₂ into active species. Especially, the synthesis of PIN catalysts is a one-step simple polymerization between benzyl bromide and bipyridine in air. The metal-free heterogeneous feature, the high selectivity, the mild conditions (60 °C, 1 h), and the facile preparation of catalyst make current selective oxidation attractive.

Introduction

Selective oxidation of sulfides and alcohols is an important process in the catalysis community with many applications ranging from organic synthesis to industrial fine-chemical production.¹⁻⁵ Traditionally, strong oxidizing agents such as trifluoroacetic acid, concentrated HNO₃-H₂SO₄, iodic acid, potassium permanganate, potassium dichromate, and other hypervalent metal salts, have typically been used for those oxidations or oxidative dehydrogenations.⁶⁻⁷ However, those processes often require excess amounts of oxidants, need corrosion-resistant instruments, suffer from the production of poisonous heavy metal ions, and are characterized by over-oxidation as a result of the uncontrolled activity. In this regard, hydrogen peroxide (H₂O₂) is a mild and green source of oxygen, with water as the only by-product, and various H₂O₂-based catalysts have been already developed for selective oxidations.

In general, metal-involved catalysts are used, and they function by activating either H₂O₂ or organic reactants.⁸⁻⁹ The famous Fenton system is such a process, with Fe²⁺-mediated H₂O₂ splitting into •OH radicals active species for the oxidative hydroxylation of benzene into phenol.¹⁰⁻¹² The formation of reactive radicals like •OOH is also possible during H₂O₂ decomposition. On the other hand, metal catalysts may start with the activation of organic molecules.¹³⁻¹⁵ In the oxidation of

sulfides (R₂S), for example, an electron transfer between R₂S and a metal catalyst can occur and lead to a reactive R₂S^{•+} intermediate that is ready to be oxidized by H₂O₂.¹⁶ Although metal catalyst-H₂O₂ systems have been thoroughly studied in past decades, there have been only limited advances in developing heterogeneous metal-free catalysts for selective oxidation.¹⁷⁻²⁰ From the standpoint of sustainable chemistry and clean catalysis, the design of heterogeneous metal-free catalysts toward selective oxidation is highly attractive but difficult.

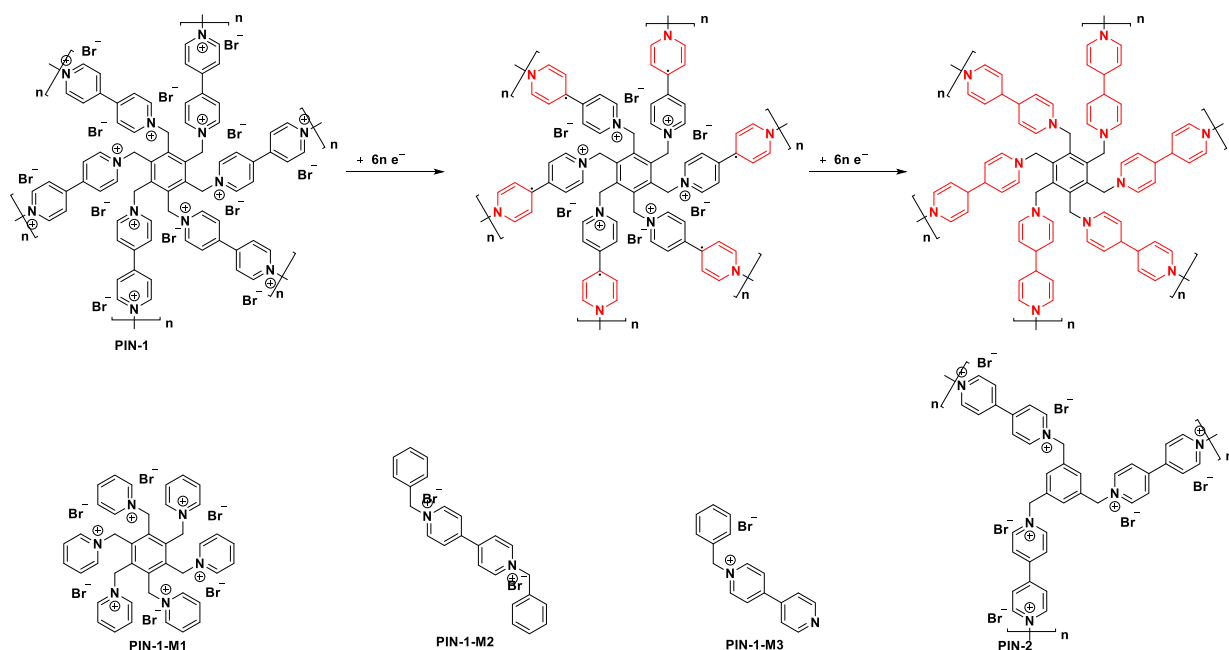
In this contribution, we introduce a class of heterogeneous viologen catalysts for metal-free and selective oxidation of sulfides and alcohols with good performance and activity. Dialkyl viologens (N,N'-dialkyl-4,4'-bipyridinium dihalides, V²⁺) as electron acceptors have been widely studied in electrochemistry because of their inherent redox reactions (V²⁺ ↔ V^{•+} ↔ V⁰).²¹⁻²² Those reversible redox processes can be promoted chemically, photochemically, or electrochemically without side reactions.²³⁻²⁷ The redox and reactive behaviours of viologens alerted us to their potential as catalysts for selective oxidations. In an unexpected experiment, we observed a photoexcited color change of polymerized ionic networks (PINs) (note: viologen radical cations usually are blue in color); and a careful investigation of their chemical structure revealed that PINs are actually highly cross-linked viologens with abundant 4,4'-bipyridinium fragments (**Figure 1** and **Scheme 1**).²⁸⁻²⁹ A detailed exploration of PINs-mediated selective oxidation (control oxidation, reaction optimization, oxidation kinetics, mechanism study, and substrate scope) was

^a School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China. E-mail: chemistryzpf@sjtu.edu.cn

^b Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, USA

^c Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA. E-mail: dais@ornl.gov

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Scheme 1. Chemical structures of polymerized ionic networks and model molecules.

then carried out. Finally, an efficient, simple, mild, and heterogeneous access for metal-free oxidations was highlighted.

Results and Discussion



Figure 1. Pictures of PIN-1 in dark or UV conditions.

A series of PINs with six 4,4'-bipyridinium cations per repeating unit were prepared by an S_N2 nucleophilic substitution between hexakis(bromomethyl)benzene and 4,4'-bipyridine.²⁹ The approach combined the ionization and polymerization of 4,4'-bipyridine in one process. All PINs are viologen-based solids that are insoluble in solvents. In contrast, viologen molecules are soluble and highly toxic. For example, paraquat (N, N'-dimethyl-4,4'-bipyridinium dichlorides, a well-known viologen) is one of the most widely used herbicides worldwide.³⁰ Thus, PINs may serve as safer viologen catalysts.

X-ray diffraction (XRD) of PIN-1 showed two broad peaks around 19° and 38° . Therefore, the PIN-1 catalyst is amorphous material (Figure S1). To study the porous nature of PIN-1 catalyst, N_2 sorption measurement at 77K was taken out (Figure S2). The PIN-1

catalyst afforded a limited surface area of $2 \text{ m}^2 \text{ g}^{-1}$. It is bulky material without abundant pores. Meanwhile, the SEM image of PIN-1 showed that the catalyst was composed of aggregations of irregular particles around $1 \mu\text{m}$, a typical morphology of polymer materials from solution participation (Figure S3).

The selective oxidation of methyl phenyl sulfide (MPS) to methyl phenyl sulfoxide (MPSO) by 30% H_2O_2 was selected as a model reaction.³¹⁻³³ No products were observed in an initial blank run (Table 1, Entry 1). Then, with PIN-1 as a catalyst, a good rate of conversion (88%) of MPS with a high selectivity for MPSO (98%) was obtained (Table 1, Entry 2). The H_2O_2 selectivity is 74% based on titration. It is clear, and interesting, that PIN-1 as a metal-free catalyst can promote liquid-phase selective oxidation. To explore which exact group is responsible for the activity, several model molecules were prepared. When PIM-1-M1, an ionic model with six pyridinium cations, was used in the process, the oxidation did not accelerate (Table 1, Entry 3). This result suggested that the 4,4'-bipyridinium fragment might contribute to the catalytic activity. Then, a control oxidation of MPS by PIM-1-M2 (N, N'-dibenzyl-4,4'-bipyridinium dibromide) was carried out, and a moderate conversion (27%) of MPS was obtained (Table 1, Entry 4), providing evidence that the viologen motif indeed promoted the oxidation. To further confirm the active site, single-substituted 4,4'-bipyridinium bromide (PIM-1-M3) was designed; but it did not function in this oxidation (Table 1, Entry 5). We attribute its failure to the poor ability of PIM-M3 to accept electrons, which at the same time revealed the necessity of the double substituted 4,4'-bipyridinium structure for catalysis.

Then, PIN-2 with a lower-density viologen structure was evaluated, and the conversion of MPS significantly decreased (16%), suggesting the vital role of the viologen structure in oxidation (Table 1, Entry 6). Moreover, the catalytic performance somewhat followed the amount of PIN-1 used in

the oxidation (1, 2.5, 3.5, 5, 7.5, 10, 15, 20 mg). The decreased amount of PIN-1 significantly affect the MPS conversion, revealing the key role of PIN-1 in current oxidation (Table S1, Figure S4). In addition, a control process without 30% H₂O₂ afforded no products, showing that 30% H₂O₂ was acting as an oxidant to incorporate oxygen into the sulfide (Table 1, Entry 7).

When ethanol (0.5 mL), an •OH radical scavenger, was added, the oxidation of MPS still occurred, a result that excluded a pathway via oxidation mediated by •OH radicals (Table 1, Entry 8).³⁴ To inquire the role of light in catalysis, a control oxidation was performed in dark. A high conversion of MPS (93%) with MPSO as primary product was obtained, indicating that the electron-transfer of PIN-1 was not initiated by light (Table 1, Entry 9). Then, we carried out the oxidation of MPS in the presence of NaBr with the aim of clarifying the role of Br⁻ anions. It is clear that no products were detected (Table 1, Entry 10). When the PIN-1 catalyst was treated with Cl⁻ for ion-exchange, the MPS conversion decreased from 88% to 11%. Those data suggested that the oxidation activity originates from the viologen cation of PIN-1 with Br⁻ as a co-catalyst.

Table 1. Selective oxidation of methyl phenyl sulfide by PINs-based catalysts.^a

Entry	Catalyst	Solvent	Conv.	Selectivity	
				MPSO	MPSO ₂
1	—	CH ₃ CN	2%	—	—
2	PIN-1	CH ₃ CN	88%	98%	2%
3	PIN-1-M1	CH ₃ CN	2%	—	—
4	PIN-1-M2	CH ₃ CN	27%	97%	2%
5	PIN-1-M3	CH ₃ CN	2%	—	—
6	PIN-2	CH ₃ CN	16%	>99%	—
7 ^b	PIN-1	CH ₃ CN	—	—	—
8 ^c	PIN-1 + Ethanol	CH ₃ CN	48%	93%	7%
9 ^d	PIN-1 (In dark)	CH ₃ CN	93%	98%	—
10	NaBr	CH ₃ CN	1%	—	—
11	PIN-1	CH ₃ OH	99%	97%	2%
12	PIN-1	Ethanol	88%	95%	4%
13	PIN-1	1-Butanol	98%	94%	6%
14	PIN-1	H ₂ O	86%	99%	1%

^a Reaction conditions: methyl phenyl sulfide 1 mmol, catalyst 20 mg, CH₃CN 4 mL, 30% H₂O₂ 2 mmol, 60 °C, 1 h. ^b No H₂O₂ was added in the control oxidation. ^c With 0.5 mL ethanol as an additive. ^d This run was conducted in the dark.

To study the effect of solvents, we proceeded to carry out the catalytic oxidations using water, methanol, ethanol or 1-butanol as the solvent with other conditions unchanged to assess the applicability of this methodology. Fortunately, varying the reaction media did not result in great divergent outcomes in terms of both activity and selectivity (Table 1, Entries 11-14). All the reactions process exhibited high reactivity, and a good conversion (99%) of MPS with a high selectivity for MPSO (97%) was obtained with methanol as the solvent, which is better than acetonitrile.

To study the reaction kinetics, the effect of stirring speed on oxidation was initially tested. When the stirring speed changed from 300 to 1200 rpm, no differences in the catalytic results were observed. Thus, mass transfer proved not to be rate-limiting in this process. All the catalytic oxidations were performed at a stirring speed of 1200 rpm. The evolution of the catalytic performance as a function of time and reaction temperature was studied over PIN-1 in detail (Figure 2). As shown in the curves, reaction temperature had a strong effect on this oxidation: higher temperatures promoted the reaction rate. The reaction time for 100% conversion of MPS increased from 70 min to 600 min when the reaction temperature decreased from 60 °C to 30 °C. Meanwhile, the reaction rate was proportional to the primary concentration of the initial substrate concentration, which suggests that the oxidation proceeds in a first-order reaction kinetics (Figure S5).

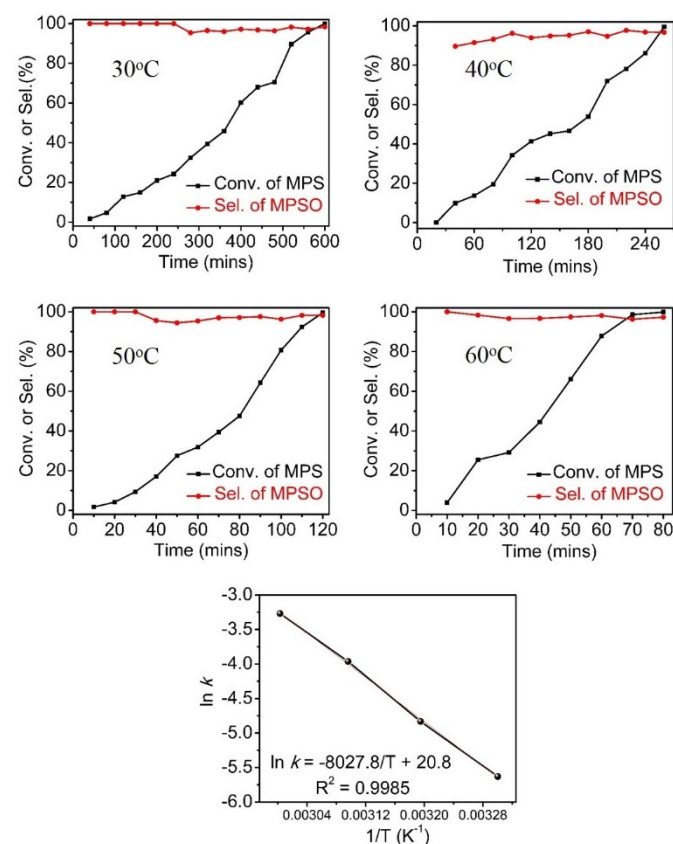


Figure 2. The conversion of MPS and selectivity for MPSO vs. time plots for the oxidation of MPS by PIN-1/H₂O₂ at different temperatures. Reaction conditions: methyl phenyl sulfide 1 mmol,

PIN-1 20 mg, 30% H₂O₂ 2 mmol, CH₃CN 4 mL, 30–60 °C. The final curve shows temperature dependence of the rate parameter in the Arrhenius equation for the PIN-1/H₂O₂ system.

During the investigation of reaction kinetics, the conversion of MPS increased almost linearly with reaction time, and the selectivity for MPSO was kept (>90%). Initial reaction rates under different reaction temperatures were determined from the kinetic curves at low conversion rates. The *k* rate constants of MPS oxidation were 0.0036 h⁻¹ (30 °C), 0.0079 h⁻¹ (40 °C), 0.0190 h⁻¹ (50 °C), and 0.0381 h⁻¹ (60 °C). The Van't Hoff approximation rule indicates that the rate constant would increase by 2–3 times if the reaction temperature increases by 10 K. Thus, this catalyst system roughly followed the Van't Hoff rule. The activation energy was then calculated using Arrhenius plots.³⁵ When the rate constant (ln *k*) was fitted with reaction temperatures (1/*T*), a straight-line plot with a correlation coefficient of 0.9985 was obtained. The activation energy (*E*_a) calculation for sulfide oxidation by PIN-1 was 66.7 kJ mol⁻¹; this moderate value suggested that this oxidation method does not require harsh reaction conditions (Figure 2).

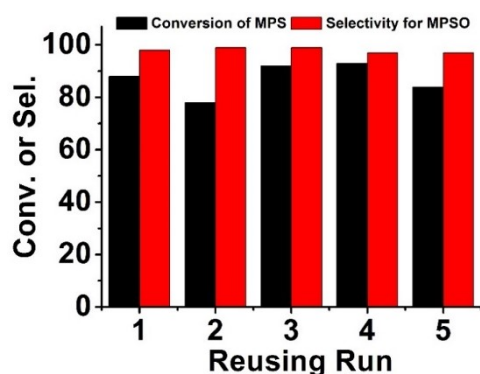


Figure 3. Selective oxidation of MPS by reused PIN-1 catalyst. Reaction conditions: methyl phenyl sulfide 1 mmol, catalyst 20 mg (Recycled), CH₃CN 4 mL, 30% H₂O₂ 2 mmol, 60 °C, 1 h.

To study the stability of PIN-1, the reaction mixture was easily separated by centrifugation, and fresh reactants with H₂O₂ were added into the reactor for next run. The PIN-1 catalyst can be used at least five times without significant loss of activity or selectivity (Figure 3). After the oxidation of MPS by PIN-1 (Reaction details: methyl phenyl sulfide 1 mmol, catalyst 20 mg, methanol 4 mL, 30% H₂O₂ 2 mmol, 60 °C, 1 h), the solid catalyst was filtered and the solution was concentrated for element analysis. Based on the amount of PIN-1 catalyst, the leaching of nitrogen is negligible (<1%), while around 1.7% bromide species were detected in the solution. Moreover, the oxidation was almost stopped if the PIN-1 solid was removed by a hot filtration (Figure S6).

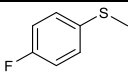
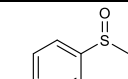
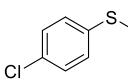
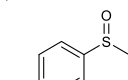
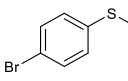
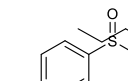
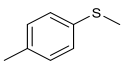
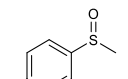
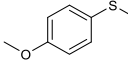
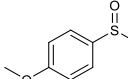
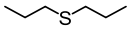
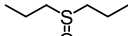
Meanwhile, we performed more characterization studies between the recycled and fresh catalysts. As shown in the SEM images, both original and reused samples were composed of irregular particles around 1 μm, which were aggregated together, a typical morphology of polymer catalysts from solution participation (Figure S3). We also carried out the FTIR spectra. Those characteristic peaks for fresh and reused PIN-1 were similar (Figure S7). Weakened zone of the absorption peaks around 3000 cm⁻¹ for the PIN-1 was

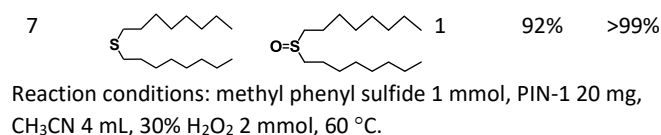
attributed to the characteristic peak of dipyriddy C-H stretching band. It might result from the chemical structure change from the 4,4'-bipyridine to 1,1',4,4'-tetrahydro-4,4'-bipyridine. Those results reveal that PIN-1 is indeed catalyzing the oxidation process in a heterogeneous manner.

It is of great interest that PIN-1 served as a metal-free heterogeneous catalyst for selective oxidation. A possible reaction pathway was then proposed. Previous efforts have already confirmed the electron-accepting behavior of PIN-1.³⁶ In the current case, H₂O₂ transforms into active species like •O₂⁻ or •OOH by an electron transfer process with formation of viologen radical cations, and the active species then oxidized sulfide into sulfoxide. At the same time, the blue-green radical cations were oxidized back into PIN-1 by molecular oxygen, a well-known process.³⁷

To explore the scope of PIN-1/H₂O₂, catalytic oxidation of some other MPS molecules was studied under optimized conditions (Table 2). Compared with MPS, the oxidation of MPS bearing electron-withdrawing groups (-F, -Cl, -Br) at the phenyl ring took a longer time, although all three processes afforded satisfactory conversion rates and selectivity. The catalyst also worked well in the oxidation of molecule models with electron-donating groups (-CH₃, -OCH₃). For example, 4-(methylphenyl) methyl sulfide was oxidized smoothly to 4-(methylphenyl) methyl sulfoxide in 1.1 h (Conv.: 99%, Sel.: >99%). Moreover, alkyl sulfides (e.g., propyl sulfide and dioctyl sulfide) could be transformed into the corresponding sulfoxides with good yields (>97%). When the dioctyl sulfide was used as the substrate, we also separate the sulfoxide product in 92% yield as a white solid. Therefore, it seems fair to say that PIN-1 is a powerful metal-free solid catalyst for catalytic oxidation of aromatic sulfide, which is comparable to the other solid catalysts (Table S2).

Table 2. Selective oxidation of various sulfides by the PIN-1/H₂O₂ system.

Entry	Substrate	Product	Time (h)	Conv. (%)	Sel. (%)
1			2.5	99%	95%
2			4	99%	>99%
3			4	99%	>99%
4			1.1	99%	>99%
5			1	88%	>99%
6			1	97%	>99%



A gram-scale preparation of MPSO was then investigated. To our delight, the oxidation of MPS (1.24-gram scale) carried out in the presence of PIN (100 mg) and H₂O₂ (20 mmol) in MeOH (30 mL) at 60 °C for 1 h gained MPSO in 90.6% yield. We also make a space-time yield every 20 minutes and it shown below in **Figure 4**. An isolated yield of 95% was obtained in 2 h. This catalyst performed high efficiency in the reaction. The properties give this methodology great promise for practical applications.

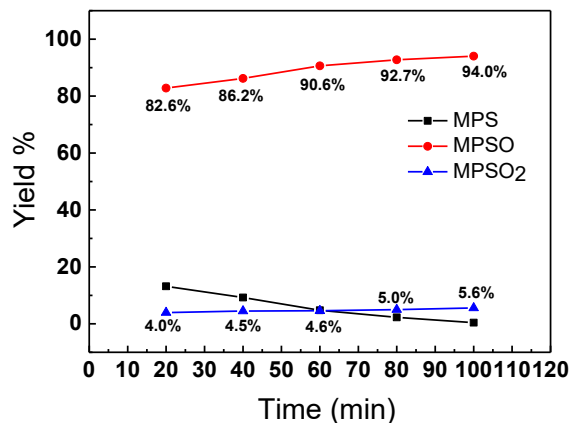
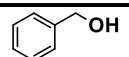
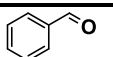
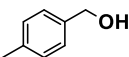
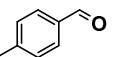
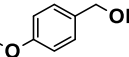
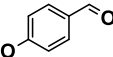
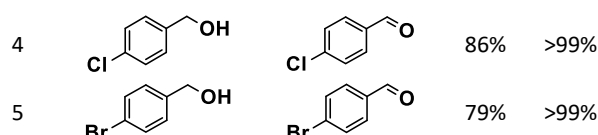


Figure 4. The yields of MPSO and MPSO₂ in the gram-scale oxidation. Reaction condition: methyl phenyl sulfide 10 mmol, 1.24 g, PIN-1 100 mg, 30% H₂O₂ 20 mmol, MeOH 30 mL, 60 °C.

The oxidative dehydrogenation of benzyl alcohols into their corresponding aldehydes is another profound process in the synthesis of fine chemicals. Encouraged by the good performance of PIN-1 in the catalytic oxidation of sulfides, we moved to the oxidation of benzyl alcohol by PIN-1/H₂O₂ (**Table 3**). Compared with sulfide oxidation, the oxidation of benzyl alcohol required a longer reaction time. In the presence of PIN-1/H₂O₂, a high conversion rate (94%) of benzyl alcohol with a high selectivity for benzaldehyde was obtained in 7 h; whereas a control run without PIN-1 offered only limited conversion (5%) of benzyl alcohol. Then, several benzyl alcohols bearing electron-donating or electron-withdrawing substituents on the phenyl ring were efficiently oxidized with high selectivity toward aldehyde products. But, the PIN-1/H₂O₂ did not work in the oxidation of an alkyl alcohol. Thus, it is clear that PIN-1 served as an active metal-free catalyst for selective oxidation of aromatic alcohols.

Table 3. Selective oxidation of benzyl alcohols by a PIN-1-Br/H₂O₂ system. ^a

Entry	Substrate	Product	Conv.	Sel.
1			94% (5%) ^b	>99%
2			82%	>99%
3			93%	>99%



^a Reaction conditions: alcohol 1 mmol, CH₃CN 4 mL, 30% H₂O₂ 2 mmol, PIN-1-Br catalyst 20 mg, 60 °C, 7 h. ^b The value from a blank oxidation without PIN-1 catalyst.

Conclusions

In summary, we have introduced a simple, efficient, and stable catalyst that enables the selective oxidation of aromatic alcohols and sulfides with good to high activities. Importantly, PIN-1 does not include metal elements and works in a heterogeneous manner, which elegantly enriches the limited library of metal-free solid catalysts available for selective oxidation. The essential point of PIN-1 lies in the abundant viologen units that were incorporated in the solid backbone. Compared with highly toxic soluble viologens, the PIN-1 solid material offers a safer catalyst.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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