

Short communication

# Improvement of the polyoxometalate's performance in the asymmetric oxidation of styrene via combined with chiral ionic liquid



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## ABSTRACT

The efficiency and enantioselectivity of polyoxometalate (POM) in the oxidation of styrene with H<sub>2</sub>O<sub>2</sub> could be improved via simply combined the POM with the chiral ionic liquids (CILs), which consist of the quaternized alkyl bromide salts (with lengths of C-8, C-12, and C-16) derived from natural chiral *S*-nicotine. The hybrids showed synergistic advantages between POM and CILs, achieving a complete conversion of styrene after 1 h of mild reaction and a relatively high selectivity for *R*-(−)-1-phenylethane-1, 2-diol with 72% yield and 96% ee. Further fluorescence analysis illustrated that CILs might serve for the enantiomeric recognition of *R*- than *S*-enantiomers.

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## 1. Introduction

The current chemistry is under increasing concerns to modify working practices and to consider the implementation of more economic and greener catalysts [1]. Polyoxometalates (POMs), known as to be an ideal case, have attracted much interest due to their physico-chemical stability, homogeneous-like behavior and lower toxicity, resulting in the extensive use of the catalysts for oxidation, esterification, alkylation, condensation, and so on [2–4]. Chirality, a phenomenon often found in daily life, had not been verified in POM-based materials until the recent ten years [5,6]. The combination of a chiral cationic group with heteropolyanions is recognized to be able to cause the formation of organic-POM hybrids with enantiomeric assemblies and thus improve their asymmetric catalytic behaviors [7]. Taking advantage of the “acid–base” principle, Luo and Li's groups developed two families of chiral amine- and diamine- [PW<sub>12</sub>O<sub>40</sub>] catalysts and showed highly enantioselective performance in the cross-aldol reaction, the Michael addition and the Diels–Alder cycloaddition under either neat or aqueous conditions [8–10]. Lou synthesized chiral amines derived from cinchonidine and immobilized them on the polyoxometalate and applied to the asymmetric aldol reaction of acetone to aldehydes with satisfying enantioselectivity [11]. These reactions suggest that the stereo effect of POM catalysts might be improved via simply combined with the chiral cationic part and become a green and stable alternative for the previous costly, noble metal catalysts.

Ionic liquids (ILs), another series of popular organics with flexible structures and properties [12], can be coupled with POMs and employed to tune the soluble and redox properties of the hybrid composites [13, 14]. ILs with a chiral nature might be synthesized as the cationic part and materialized the hybrids with a particular chiral feature. *S*-nicotine is the important byproduct of tobacco manufacture and is also a natural chiral alkaloid like cinchonidine, whose analogs have been widely used as insecticides. Previously Kitazume described a type of chirally active ionic liquid derived from the natural *S*-nicotine and used that as solvent in the enzyme-catalyzed interesterification of 4-methoxy-(1'-methyl)-benzyl alcohol and vinyl acetate (35% ee left) [15]. Recently nicotine-derived ammonium salts were taken as a highly efficient catalyst for chemical fixation of CO<sub>2</sub> into cyclic carbonates [16]. In the present work, we also prepared a series of CILs derived from optically pure *S*-nicotine with different alkyl lengths, which can be combined with the same POM anion. The objective of this work is to characterize the performance of the hybrid catalysts and discuss the role of CILs in the asymmetric oxidation of styrene.

## 2. Experimental

## 2.1. Chemicals and materials

All chemical reagents are commercially available except for the chiral ionic liquids used in this work. CILs were prepared in advance and their molecular structures are shown in Fig. 1, respectively named as [NC<sub>8</sub>] Br, [NC<sub>12</sub>] Br and [NC<sub>16</sub>] Br. The synthesis procedures referred to a reported route [17] and detailed data are described in Electronic Supporting Information (ESI).

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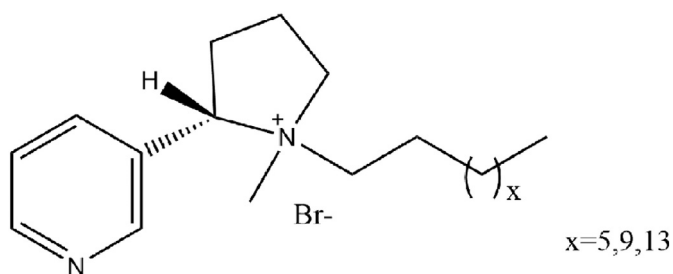


Fig. 1. The molecular structures of the prepared CILs.

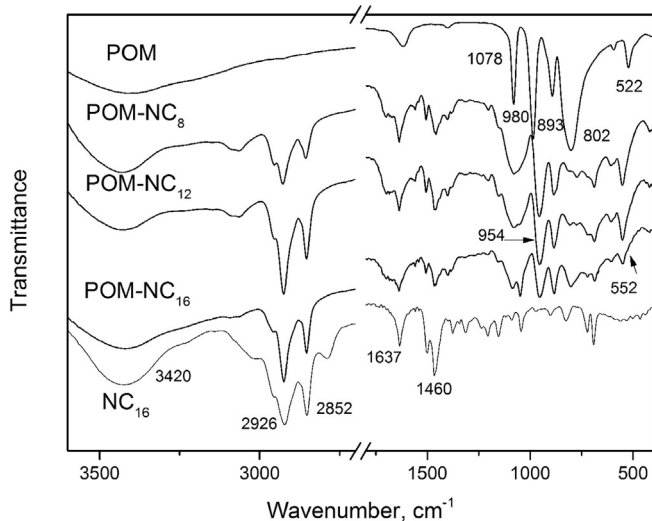


Fig. 2. FTIR spectra of POM, POM-based hybrid catalysts and NC<sub>16</sub>.

## 2.2. Preparation and application of POM–CIL hybrid catalysts

The polyoxometalate (POM)-based hybrid catalysts were prepared according to the literature [18,19]. POM-NC<sub>16</sub> is presented as an example: H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·16.5 H<sub>2</sub>O (6.65 g, 0.002 mol) was dissolved in 50 ml of H<sub>2</sub>O<sub>2</sub> (20%) and heated at 40 °C for 30 min until a colorless solution was obtained. Then, 2.19 g of [NC<sub>16</sub>] Br (0.006 mol) in vinyl acetate (30 ml) was added dropwise to the solution with stirring for 8 h. The precipitate was filtered and washed with distilled water, then dried in vacuum at 80 °C for 12 h. Finally a solid yellow catalyst was obtained. The other two catalysts were synthesized with similar procedures, named as POM-NC<sub>8</sub>, POM-NC<sub>12</sub>, and fully characterized by FT-IR, TG-DTA and AAS. The detailed catalytic experiments were described in ESI.

## 3. Results and discussion

The combination of CILs and POM can be confirmed by the FT-IR, TG-DTA and MAS NMR. Here was only NC<sub>16</sub> regarded as an organic example (in Fig. 2) because other CILs in this work have similar chemical structure and shows similar IR spectra. In view of the organic cations, the strong and broad IR band at 3420 cm<sup>-1</sup> was attributed to the stretching vibration of N–H...N. The distinct bands, including 2926, 2852, 1637 and 1460 cm<sup>-1</sup>, exhibited the characteristics of –CH<sub>3</sub>, C=N, C=C. Meanwhile, IR bands at 1078, 980, 893 and 802 cm<sup>-1</sup> corresponded to the characteristic skeletal vibrations of the polyoxometalate oxoanions, respectively as  $\nu_{as}$  (P–O),  $\nu_{as}$  (W=O), and  $\nu_{as}$  (W–O–W) in a shared corner octahedral, as well as  $\nu_{as}$  (W–O–W) in a shared edge octahedral [20,21]. Another band at 522 cm<sup>-1</sup> shifting into 552 cm<sup>-1</sup> was supposed to be identified into W–O–O– vibration in the presence of peroxy specie in {PO<sub>4</sub>[W(O)<sub>2</sub>(O<sub>2</sub>)]<sub>4</sub>}<sup>3-</sup> [22]. Even an obvious red shift occurred from 980 cm<sup>-1</sup> to 954 cm<sup>-1</sup>, implying the formation of the strong ionic linkage between the amide-cation and the heteropolyanion.

The TG-DTA for the catalysts is shown in Fig. 3. Three hybrids, with the same starting quantity, had the amount of crystallized water (5 ~ 6%) lost between 100 and 120 °C, and they were stable up till to 200 °C. The distinct weight loss in the range of 250 to 300 °C and 350 to 400 °C is respectively due to the decomposition of alkyl chains and nicotine components. And the more pronounced weight loss was observed on the samples with the longer alkyl organics (28% ~ 33%). The solid nature of the hybrids (mp > 250 °C) is suggested to arise from the extended hydrogen bonding networks, as well as the strong interaction between the CIL cation and the high valence POM anion.

The <sup>31</sup>P MAS NMR spectra of POM-based ILs catalysts are shown in Fig. 4. The peaks from 0 to –15.0 ppm can be assigned to heteropolytungstophosphates with the ratio of P / W from 1/2 to 1/12 [23]. The catalysts containing more active oxygen show the decreasing P / W ratio. It is clear that the relatively pure catalyst can be got and appears only one component. The neighboring species at about –3.2, –5.0 and –6.1 ppm might be due to species with the identical higher P / W ratio [24] and the tiny migrations also indicated the impacts of different alkyl ionic liquids on the phosphorous electro-magnetic environment.

Through the selective oxidation, styrene became the precursors to phenyloxirane, benzaldehyde and 1-phenylethane-1, 2-diol [25]. Phenyloxirane formed by epoxidation in the first step could be quickly converted into benzaldehyde via the nucleophilic attack of H<sub>2</sub>O<sub>2</sub> [26]. The hydrolysis of phenyloxirane to form 1-phenylethane-1, 2-diol is probably caused by the presence of amounts of water in 30% H<sub>2</sub>O<sub>2</sub>. The detailed oxidation results were listed in Table 1. In contrast to POM–CILs, IL itself was inactive and H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> only gave a 25.2% conversion, yield of phenyloxirane (62.6%), illustrating the formation of synergistic effect of the POM and CILs. Three hybrid catalysts proved to be catalytically active with the conversion of styrene, reaching 56–

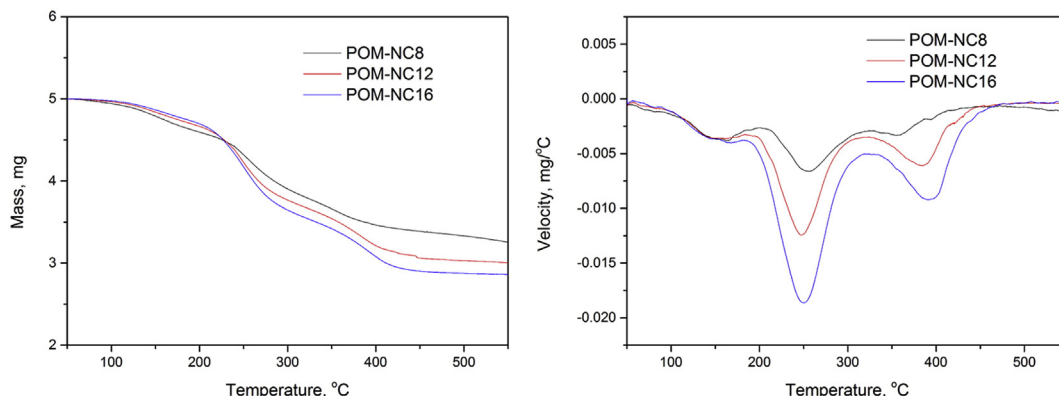


Fig. 3. TG-DTA of POM-based hybrid catalysts.

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