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A novel heteropolyanion-based amino-containing cross-linked ionic copolymer catalyst for epoxidation of alkenes with H_2O_2

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ABSTRACT

A heteropolyanion-based cross-linked ionic copolymer was prepared by the anion-exchange of a newly task-specific designed amino-containing ionic copolymer with a Keggin heteropolyacid, and characterized by FT-IR, SEM, TG, XRD, UV–vis, ESR, ¹H NMR, and elemental analysis. Its catalytic activity was evaluated in the epoxidation of alkenes with aqueous H₂O₂. The resultant heteropolyanion-based ionic copolymer is revealed to be a highly efficient heterogeneous catalyst for epoxidation of alkenes with H₂O₂, adding the advantages of convenient recovery and steady reuse.

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1. Introduction

Epoxidation of alkenes with H₂O₂ has been extensively investigated over the catalysts of heteroatomic molecular sieves [1], transition metal compounds [2], organometallic complexes [3], and polyoxometalates (POMs) [4,5]. Heterpolyacids (HPAs) are a family of POMs, and the tungsten-containing HPAs, typically the Venturello-Ishii $\{PO_4[WO(O_2)_2]_4\}^{3-}$ species, have attracted much attention for a long time as the effective catalysts for the H₂O₂-based epoxidation of alkenes [6]. However, HPAs always cause homogeneous reactions because of their good solubility in polar/oxidative media, resulting in the difficulty of catalyst isolation. Thus, heterogeneous HPA catalysts are a promising option, and various strategies, including attaching HPAs to porous supports [7–9], biphasic technology and phase-transfer catalysis [10,11], have been developed. Though good activity was achieved in those cases, most of them still bear some drawbacks like the slow reaction speed, leaching of active species, low catalyst recovery rate, or high cost. A new strategy for catalyst preparation to overcome the above problems is therefore highly desirable.

The organic–HPA hybrids, obtained by the modification of HPAs with organic blocks, have attracted great research interest due to their diverse chemical structures and improved catalytic behaviors [12,13]. A topic of recent interest in this context is the design and

application of HPA-based ionic liquid (IL) hybrids as the catalysts for organic syntheses [14], and some thermal/solvent-responsive HPA-based IL hybrids have been reported [15,16]. We recently prepared a series of HPA-based ionic hybrids by combining organic IL cations with Keggin heteropolyanions, and the resulting ionic solids turned out to be effective and recyclable catalysts for acid-catalyzed or oxidative organic transformations [17,18].

More recent studies have shown that ionic copolymers containing IL units are capable of acting the bifunctions of both ILs and polymers [19-21]. Moreover, owing to the features of high thermal stability, easily shaping, corrosion resistance, and the variety of structures available, polymer matrices are excellent supports to entrap POMs for applications in heterogeneous catalysis [22]. For example, poly(nisopropylacrylamide) polymer with a quaternary ammonium and phosphotungstate anion (PW₁₂O₄₀³⁻) can be used as a temperature-responsive catalyst for the oxidation of alcohols, causing thermoregulated formation of stable emulsion species at 90 °C in water [23]. Water-soluble HPA-conjugated chitosan matrix was revealed to be an effective catalyst for the triphase epoxidation of allylic alcohols [24]. Also noticeably, the amino groups tethered to IL cations have been demonstrated to be the catalytic promoters for HPA active sites in epoxidations due to the electron transfer from aminos to HPA frameworks [18]. Accordingly, it is rational to design and prepare a HPA-based amino-containing ionic copolymer catalyst for epoxidation of alkenes with hydrogen peroxide by combining amino-functionalized IL copolymers with HPAs with a more structural stability, because of the involvement of a polymeric framework in the catalyst.

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