



Heteropolyanion-paired cross-linked ionic copolymer: An efficient heterogeneous catalyst for hydroxylation of benzene with hydrogen peroxide

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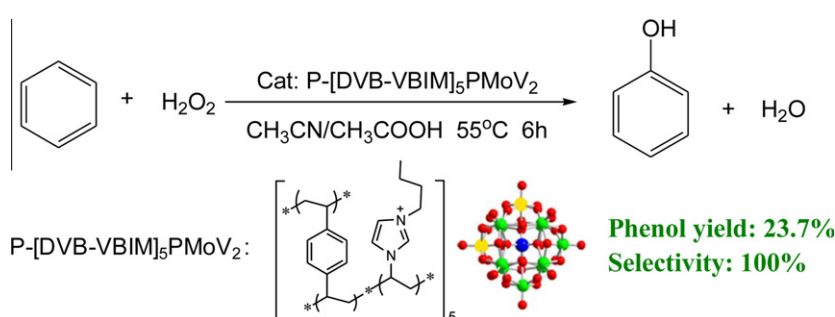
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HIGHLIGHTS

- ▶ A new heteropolyanion-based cross-linked ionic copolymer catalyst is prepared.
- ▶ The ionic copolymer shows high activity for hydroxylation of benzene with H₂O₂.
- ▶ The ionic copolymer is a heterogeneous catalyst with easy and steady reuse.
- ▶ High surface area and intramolecular charge transfer explain its performance.

GRAPHICAL ABSTRACT



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ABSTRACT

A heteropolyanion-based cross-linked ionic copolymer was prepared by the anion-exchange of heteropolyacid (HPA) H₅PMo₁₀V₂O₄₀ with polymeric ionic liquid (PIL) poly(divinylbenzene-3-*n*-butyl-1-vinylimidazolium)Br, and characterized by FT-IR, UV-vis, XRD, TG, SEM, elemental analysis and BET surface areas. The characterization results show that the ionic copolymer is an amorphous HPA salt of PIL-cation with a considerable thermal stability, high surface area and large pore volume. Further, the ionic copolymer is revealed to be a highly efficient heterogeneous catalyst for hydroxylation of benzene with H₂O₂ to phenol, showing high activity, convenient recovery and steady reuse. The excellent performance of the novel porous HPA-based copolymer catalyst is discussed in relation to its textural property and intramolecular charge transfer behavior.

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1. Introduction

As an important chemical intermediate, phenol is mainly produced by the three-step cumene process with low atom utilization, high energy consumption and environmental pollution [1,2]. Nowadays, the green process of direct hydroxylation of benzene into phenol has attracted great interest using clean oxidants like N₂O [3], O₂ [4,5], and H₂O₂ [6], as well as the H₂-O₂ system with Pd-based composite membrane reactors [7,8]. For hydroxylation of benzene with H₂O₂, metal oxides [9], molecular sieves (e.g. TS-

1, Ti-MS1 and V-MCM-41) [10–12], and polyoxometalates (POMs) [13] have been reported as the catalysts. It is known that polymeric catalysts have got versatile utilizations in acid-catalyzed or oxidation reactions [14,15], but only very few applications in hydroxylation of benzene have been attempted so far [16]. Therefore, to explore new and highly efficient polymeric catalysts for hydroxylation of benzene is an open and interesting topic.

Ionic liquids (ILs) are well-known reaction media/catalysts, and a variety of functionalized ILs have been developed with functional groups tethered to cations or anions [17–21]. On the other hand, the V-containing heteropolyacids (HPAs), a kind of POMs, have shown high catalytic activity towards phenol in hydroxylation of benzene [22,23]. Indeed, HPA-anions have been used as counter

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anions for ILs [24,25], and some HPA-IL ionic compounds have been prepared and employed as inorganic–organic hybrid catalysts [26,27]. Very recently, we have prepared a series of HPA-based ILs by combining functionalized IL-cations with Keggin heteropolyanions for heterogeneous organic transformations [28–33]. However, the insoluble HPA salts of IL-cations usually become dissolvable in the process of hydroxylation of benzene with excess aqueous H_2O_2 . Only the HPA-IL catalyst with a specially design IL-cation could cause a heterogeneous H_2O_2 -based hydroxylation of benzene [33].

It is worthwhile to note that polymeric ionic liquids (PILs) have been used as novel catalysts for more and more organic syntheses with advantageous of enhanced stability and improved processability [34,35]. Taking account of the well-known high activity of V-containing heteropolyacid for hydroxylation of benzene and the improved solid framework structure of a polymeric IL-cation, we think it rational to try a HPA-PIL hybrid catalyst for H_2O_2 -based hydroxylation of benzene, which have not been reported as yet. In this study, we synthesize a new porous HPA-based polymeric IL catalyst P-[DVB-VBIM]₅PMoV₂ by pairing the polymeric IL-cation P-[DVB-VBIM]⁺ with V-containing Keggin HPA-anion (PMoV₂) (Scheme 1). The resulting solid-state HPA-PIL hybrid catalyst is revealed to cause a liquid–solid heterogeneous oxidation system for hydroxylation of benzene with H_2O_2 , showing high activity and good recyclability.

2. Experimental

2.1. Materials and methods

All chemicals were analytical grade and used as received. FT-IR spectra were recorded on a Nicolet 360 FT-IR instrument (KBr discs) in the 4,000–400 cm^{-1} region. Elemental analyses were performed on a CHN elemental analyzer (FlashEA 1112). XRD patterns were collected on the Bruker D8 Advance powder diffractometer using Ni-filtered Cu K α radiation source at 40 kV and 20 mA, from 5° to 50° with a scan rate of 2°/min. Before measurements the samples were dried at 100 °C for 2 h. ¹H NMR spectra were measured with a Bruker DPX 500 spectrometer at ambient temperature in D⁶-DMSO using TMS as internal reference. BET surface areas were measured at the temperature of liquid nitrogen using a Micromeritics ASAP2010 analyzer. The samples were degassed at 150 °C to a vacuum of 10^{−3} Torr before analysis. SEM image was performed on a HITACHI S-4800 field-emission scanning electron microscope. TG analysis was carried out with a STA409 instrument in dry air at a heating rate of 10 °C/min.

2.2. Preparations and characterizations of catalysts

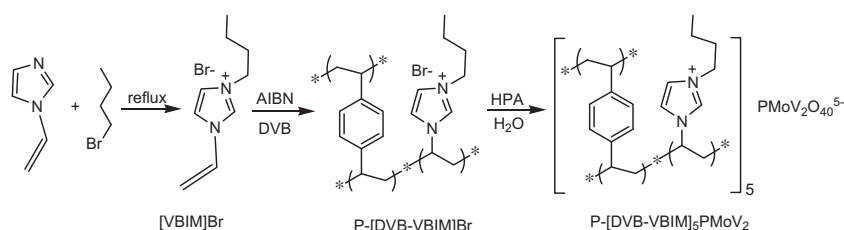
The Keggin-structured double V-containing POM H₅PMo₁₀V₂O₄₀ (H₅PMoV₂) was prepared according to our previous literature [36]. In detail, MoO₃ (16.59 g, 0.115 mol) and V₂O₅ (2.1 g, 0.0115 mol) were added to deionized water (250 mL), which was heated up to 120 °C for reflux under vigorously stirring with a water-cooled

condenser. The concentrated H₃PO₄ (85 wt.%, 1.33 g, 0.0115 mol) in water (10 mL) was drop-wise added into the above mixture within 30 min. With a further stirring for 24 h, a clear orange-red solution appeared, and after cooling of the solution to room temperature, the orange fine powder was got by a vacuum drying of the solution at 50 °C for 24 h. The final product H₅PMoV₂ was obtained by re-crystalizing the powdered solid in deionized water. The single V-containing POM H₄PMo₁₁VO₄₀ (H₄PMoV) was synthesized based on above procedures, using the raw materials of MoO₃ (17.79 g, 0.121 mol), V₂O₅ (1.02 g, 0.0055 mol) and 85 wt.% aqueous solution of H₃PO₄ (1.29 g, 0.0112 mol).

The IL precursor 3-*n*-butyl-1-vinylimidazolium bromide ([VBIM]Br) was synthesized consulting the previous literature [37]. Bromobutane (15.07 g, 0.11 mol) and 1-vinylimidazole (9.4 g, 0.1 mol) were added to a 100 mL round-bottomed Schlenk flask equipped with a magnetic stirrer. After stirred at 70 °C for 24 h under the protection of nitrogen, the reaction mixture was cooled to room temperature. Then the top liquid was poured out, and the solid residue was washed three times with diethyl ether and dried at 60 °C for 12 h under vacuum. Yield: 85%. Elemental analysis Calcd: C, 46.75 wt.%; N, 12.12 wt.%; H, 6.49 wt.%. Found: C, 46.70 wt.%; N, 12.13 wt.%; H, 6.53 wt.%. ¹H NMR (500 MHz, D⁶-DMSO, TMS); δ 9.765 (s, 1H), 8.281 (s, 1H), 8.001 (s, 1H), 7.357 (m, 1H), 6.031 (m, 1H), 5.419 (m, 1H), 4.239 (t, 2H), 1.816 (m, 2H), 1.289 (m, 2H), 0.897 (t, 3H).

Preparation of heteropolyanion-paired cross-linked polymeric IL P-[DVB-VBIM]₅PMoV₂ is sketched in Scheme 1. DVB (divinylbenzene) (7.23 g, 0.055 mol), [VBIM]Br (11.55 g, 0.05 mol), and AIBN (azobisisobutyronitrile) (0.9 g, 0.0055 mol) were dissolved in ethyl alcohol (150 mL) in a three-necked flask under nitrogen atmosphere. The mixture was maintained at 70 °C for 48 h under reflux and stirring. The white solid was collected by filtration and washed respectively with acetone (30 mL) and methanol (30 mL) for three times. After a vacuum drying at 50 °C for 24 h, P-[DVB-VBIM]Br was obtained. (Yield: 86%. Elemental analysis Found: C, 86.15 wt.%; N, 1.38 wt.%; H, 8.81 wt.%). Afterwards, P-[DVB-VBIM]Br (1.81 g, 0.005 mol) was added to 250 mL of the ethyl alcohol solution of H₅PMo₁₀V₂O₄₀ (1.73 g, 0.001 mol), and the mixture was stirred at room temperature for 72 h. The created precipitate was filtered, washed with water (200 mL) for three times, and dried in vacuum at 80 °C to obtain the final product P-[DVB-VBIM]₅PMoV₂ (Yield: 92%. Elemental analysis Found: C, 51.78 wt.%; N, 3.18 wt.%; H, 5.65 wt.%). P-[DVB-VBIM]₄PMoV (PMoV: PMo₁₁VO₄₀^{4−}) was prepared according to similar procedures using H₄PMoV as the raw material. (Yield: 90%. Elemental analysis Found: C, 50.61 wt.%; N, 2.63 wt.%; H, 5.45 wt.%).

Poly(3-*n*-butyl-1-vinylimidazolium)₅PMoV₂O₄₀ (P-[VBIM]₅PMoV₂) was synthesized according to the literature [38]. [VBIM]Br (11.55 g, 0.05 mol) and AIBN (0.9 g, 0.0055 mol) were dissolved in ethyl alcohol (150 mL) in a three-necked flask with nitrogen protection. The mixture was maintained at 70 °C at reflux for 48 h with stirring. The produced precipitate was filtered, washed with acetone (30 mL) for three times, and then was dried in vacuum at 50 °C for 24 h to give P-[VBIM]Br. (Yield: 86%. Elemental analysis



Scheme 1. Synthesis of the porous HPA-based cross-linked polymeric IL catalyst P-[DVB-VBIM]₅PMoV₂.

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