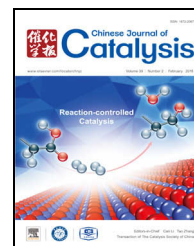


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Article

Mesoporous polyoxometalate-based ionic hybrid as a highly effective heterogeneous catalyst for direct hydroxylation of benzene to phenol

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ABSTRACT

Self-assembled mesoporous polyoxometalate-based ionic hybrid catalyst, $[PxyDim]_{2.5}PMoV_2$, was prepared by combining *p*-xylene-tethered diimidazole ionic liquid $[PxyDim]Cl_2$ with Keggin-structured V-substituted polyoxometalate $H_5PMo_{10}V_2O_{40}$. The obtained hybrid was shown to be a mesostructured and hydrophobic material with good thermal stability. In the H_2O_2 -based hydroxylation of benzene to phenol, the hybrid showed extraordinary catalytic activity and rate, and quite stable reusability. The unique hydrophobic properties and mesoporous structure of the hybrid were responsible for its excellent catalytic performance.

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1. Introduction

Phenol is among the main raw materials used in the chemical industry, including in the synthesis of resins, fungicides, preservatives, and pharmaceuticals. Industrially, phenol is produced by the three-step cumene process, which has high energy consumption and produces much environmental pollution [1]. Therefore, many attempts have been made to develop a one-step hydroxylation of benzene to phenol using different oxidants, such as O_2 [2], H_2O_2 [3], and N_2O [4], as well as H_2 - O_2 systems with Pd-based composite membrane reactors [5]. Schiff bases [6], vanadium-containing mesoporous carbon [7–11], TS-1 molecular sieves [12], Fe-based metal-organic frameworks (MOFs) [13], and polyoxometalates (POMs) [14–16] have been applied as catalysts in the environmentally

friendly H_2O_2 -based hydroxylation of benzene. Among them, V-containing POM catalysts have proven to be effective catalysts because of the relatively mild reaction conditions required for direct hydroxylation of benzene to phenol [17,18]. Unfortunately, isolating and recycling these catalysts is difficult because POMs readily dissolve in the polar reaction system. Therefore, the preparation of heterogeneous POMs for the direct hydroxylation of benzene has become an interesting and challenging task.

The immobilization of POMs onto porous supports is a commonly used strategy to heterogenize POMs catalyst [19]. However, this approach inevitably suffers from slow reaction rates and/or leaching of active sites. Recently, the modification of POMs with organic units, such as ionic liquids (ILs), organometallic complexes, organic polymers, and silica matrices, has

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been developed to prepare POM-based organic-inorganic hybrid heterogeneous catalysts [20–24]. In this context, the assembly of POMs with task-specific ionic liquid cations is a successful example that is beneficial for adjusting the solubility, redox properties, and surface microenvironment of POMs. Previously, we have reported a series of POM-based ionic hybrid catalysts prepared by combining ionic liquid cations with heteropolyanions, with the resulting ionic solids shown to be effective catalysts for the oxidation of sulfides and benzene [25–27]. Nevertheless, self-assembled ionic hybrids are non-porous and have low specific surface areas, which limit the heterogeneous catalytic activity in mass-transfer-controlled systems [28]. The direct hydroxylation of benzene using POM-based polymeric ionic hybrid heterogeneous catalysts has also been studied [29]. Despite the high specific surface areas and excellent performance obtained, complex steps and large amounts of organic solvent are required for catalyst preparation. Therefore, a simple approach to prepare a highly efficient heterogeneous POM-based catalyst with mesoporous structure and high specific surface area is required.

In contrast, it should be noted that highly hydrophobic organic frameworks in hybrid catalysts act as dynamic traps that can adsorb relatively nonpolar substrate molecules and easily desorb relatively polar product molecules [30,31]. Therefore, hydrophobic organic segments in hybrid catalysts can enhance the probability of interactions between the substrate and catalytic center, which would improve the catalytic activity and selectivity.

Accordingly, we herein report a highly hydrophobic mesoporous POM-based hybrid catalyst prepared by pairing V-containing POM anions with *p*-xylene-tethered diimidazole ionic liquid cations (Fig. 1). The catalysts not only exhibit enhanced catalytic activities for the direct hydroxylation of benzene with H_2O_2 , but also facilitate catalyst recovery from the reaction system. The excellent catalytic performances of these catalysts are mostly attributed to the contributions of their porous structures and hydrophobic microenvironments.

2. Experimental

2.1. Materials and analytic methods

All chemicals, including benzene (99.5%), acetonitrile (99.9%), acetic acid (99.8%), and dichloromethane (99.9%), were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification.

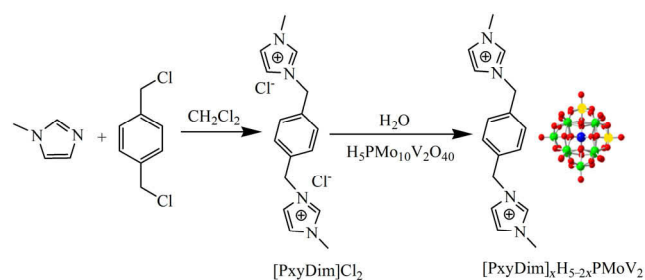


Fig. 1. Schematic preparation of ionic hybrid catalysts.

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 360 FT-IR instrument (using KBr discs) in the wavenumber region $4000\text{--}400\text{ cm}^{-1}$. Elemental analysis was performed using a CHN elemental analyzer (Vario EL cube) and inductively coupling plasma spectrometer (ICP, Jarrell-Ash 1100). X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance powder diffractometer using a Ni-filtered $\text{Cu K}\alpha$ radiation source at 40 kV and 200 mA, in the 2θ range of $5^\circ\text{--}50^\circ$ at a scan rate of $2^\circ/\text{min}$. Brunauer-Emmett-Teller (BET) surface areas were measured at the temperature of liquid nitrogen using a Micromeritics ASAP2010 analyzer. Samples were degassed at 150°C to a pressure of 10^{-3} Torr before analysis. Scanning electron microscopy (SEM) images were recorded using a Hitachi S-4800 field-emission scanning electron microscope. Thermogravimetric (TG) analysis was conducted using a STA409 instrument in dry air at a heating rate of $10^\circ\text{C}/\text{min}$.

2.2. Catalyst preparation

2.2.1. Preparation of $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$

$\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$, herein abbreviated as PMoV_2 , was prepared according to our previous work [29]. In detail, MoO_3 (16.59 g, 0.115 mol) and V_2O_5 (2.1 g, 0.0115 mol) were added to deionized water (250 mL), and heated to reflux under vigorous stirring, using a water-cooled condenser. An aqueous solution of H_3PO_4 (1.33 g, 0.0115 mol, 85 wt%) was then added dropwise to the mixture. When the mixture became a clear orange-red solution, it was cooled to room temperature. $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ was obtained as an orange-red powder after evaporating the solution to dryness and purification by recrystallization.

2.2.2. Preparation of ionic liquid precursors

Dicationic ionic liquid precursor $[\text{PxyDim}]\text{Cl}_2$ was prepared as follows. Methylimidazole (0.21 mol) and α,α' -dichloro-*p*-xylene (0.10 mol) were dissolved in dichloromethane (50 mL) at 35°C under a nitrogen atmosphere and stirred for 48 h. The solvent was then removed by distillation and the residue was washed with THF ($3 \times 30\text{ mL}$). After drying under a high vacuum, $[\text{PxyDim}]\text{Cl}_2$ was obtained as a white solid in 95% yield.

Analogous ionic liquid $[\text{EthDim}]\text{Cl}_2$ was prepared according to a literature procedure [20]. Methylimidazole (0.21 mol) and 1,2-dichloroethane (0.10 mol) were dissolved in isopropanol (50 mL) at 80°C under a nitrogen atmosphere and stirred for 48 h. On reaction completion, the solvent was removed by distillation, and the product was dried under high vacuum to afford $[\text{EthDim}]\text{Cl}_2$ as a colorless liquid in 83% yield. Ionic liquid $[\text{ButDim}]\text{Cl}_2$ was synthesized using the same method. $[\text{BMim}]\text{Cl}_2$ was synthesized according to a literature procedure [29].

2.2.3. Preparation of polyoxometalate-based ionic hybrids

Polyoxometalate (POM)-based ionic hybrids were prepared by reacting the ionic liquid precursors with PMoV_2 . In a typical procedure, $[\text{PxyDim}]\text{Cl}_2$ (5.0 mmol) and PMoV_2 (2.0 mmol) were separately dissolved in deionized water (2.0 mmol). The

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