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Hydroxylation of Benzene to Phenol by H_2O_2 over an Inorganic–Organic Dual Modified Heteropolyacid[☆]

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ABSTRACT

Various catalysts, including the heteropolyacid (HPA) $H_4PMo_{11}VO_{40}$, its cesium salts, and inorganic–organic dual modified HPA catalyst, were prepared and characterized by Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (^{13}C NMR), N_2 adsorption, acid–base titration, electron spin resonance (ESR) and X-ray diffraction (XRD) techniques as well as elemental analysis. These prepared catalysts were used in the hydroxylation of benzene to phenol by H_2O_2 as oxidant. The inorganic–organic dual modified HPA $Cs_{2.5}(MIMPS)_{1.5}PMo_{11}VO_{40}$, prepared by partially exchanging Cs^+ with protons in $H_4PMo_{11}VO_{40}$ and followed by the immobilization of 3-(1-methylimidazolium-3-yl)propane-1-sulfonate (MIMPS), led to a liquid–solid biphasic catalysis system in the hydroxylation, which showed the best catalytic performance in terms of reusability and catalytic activity. The high reusability of $Cs_{2.5}(MIMPS)_{1.5}PMo_{11}VO_{40}$ in the heterogeneous hydroxylation was probably due to its high resistance in leaching of bulk HPA into the reaction medium. The slightly enhanced catalytic activity for the catalyst was due to the acid sites available from MIMPS beneficial to the hydroxylation.

1. Introduction

Phenol, one of the most important basic chemicals, is commercially produced by the so-called cumene process in the chemical industry, which is a low atom utilization and a high energy consumption process. One-step hydroxylation of benzene to phenol attracts more and more attention. There are three main pathways for the one-step hydroxylation of benzene. Benzene can be selectively oxidized to phenol in gas phase over zeolite catalysts like Fe-ZSM-5 using N_2O as oxidant [1,2]. However, the oxidant N_2O is not readily available, besides the easy deactivation of the used zeolite-based catalyst due to coke formation [2].

The gas-phase oxidation of benzene can be also converted into phenol by the *in-situ* formed H_2O_2 from the reaction of O_2 with H_2 in a Pd-based composite membrane reactor, but its low selectivity for phenol and the difficult scale-up of the membrane reactor hamper the process to be industrialized [3,4]. Recently, the liquid-phase hydroxylation of benzene to phenol using H_2O_2 as an environmentally benign oxidant has attracted great attention because H_2O_2 is cheap, readily available, easy to handle, and gives water as the only by-product [5]. Therefore, various heterogeneous catalysts have been applied to the hydroxylation of benzene to phenol by H_2O_2 [6–8]. However, these applied catalysts cannot simultaneously possess a reasonable activity for the conversion of benzene and a high selectivity for phenol, resulting in the rather low yield of phenol. Vanadium containing heteropolyacids (HPAs) have been proven to be effective catalysts for the hydroxylation of benzene to phenol [9–17]. Unfortunately, pure HPAs utilized in bulk form, which can be dissolved in a polar reaction medium, have some drawbacks such as difficulty for catalyst separation and recovery. Therefore, the immobilization of HPAs onto porous supports becomes the commonly used method to heterogenize the HPA catalysts. However, the catalyst preparation by the immobilization of HPAs onto porous supports is generally complicated [18], and the prepared catalysts usually show low activities in the hydroxylation of benzene to phenol and the leaching of active species inevitably takes place during the hydroxylation [19,20]. Apparently, the heterogeneous hydroxylation of benzene by H_2O_2 catalyzed by HPA-based catalysts still remains a challenge.

Recently, the design and preparation of inorganic–organic hybrid catalysts based on HPAs have gained great attention [21–23]. The highly hydrophobic organic segments in the hybrid catalysts can encapsulate relatively nonpolar substrate molecules as a result of hydrophobic interactions but easily release relatively polar product molecules. Thus, the organic segments in the hybrid catalysts act as a dynamic trap to enhance the probability of an interaction between the substrate and the catalytic center [24,25], improving their catalytic activity and selectivity. On the other hand, the inorganic segments (such as Cs^+) in the hybrid catalysts can significantly tune the crystalline nature and high lattice energy of HPAs due to strong ionic interactions [24,25]. Therefore, water soluble pure HPAs can be transformed into insoluble HPA salts in a polar reaction medium *via* inorganic modification, which makes it convenient to recover and reuse HPA salts as catalysts. Even though there

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has been plenty of work on the acidic cesium salts of $H_3PW_{12}O_{40}$ as heterogeneous catalysts in acid-catalyzed reactions because of their high catalytic activities [25–28], little work has been conducted on the application of the HPA salts to the hydroxylation of benzene to phenol.

In the current study, inorganic–organic dual modified HPA catalysts were prepared. The Keggin structure V-containing $H_4PMo_{11}VO_{40}$ was selected as starting material because of its rich structural versatility along with well-defined physical and chemical properties. The selected HPA was sequentially ion exchanged with Cs^+ and followed by anchoring organic molecules containing sulfonic acid groups to obtain inorganic–organic dual modified HPA catalysts that were used in the hydroxylation of benzene to phenol by H_2O_2.

2. Experimental

2.1. Chemicals

All reagents with AR purity (analytical reagent grade) were purchased and used as received without further purification. Molybdenum trioxide, vanadium pentoxide, phosphoric acid (85%, by mass, aqueous solution), cesium carbonate, toluene, ether, 1,3-propanesultone, 1-methylimidazole, benzene, hydrogen peroxide (30%, by mass, solution) and acetonitrile were purchased from Sinopharm Chemical Reagent Co., Ltd. The deionized water was obtained from Millipore Milli-Q ultrapure water purification systems with the resistivity larger than 18.2 MΩ.

2.2. Catalyst preparation

The molybdovanadophosphoric heteropolyacid $H_4PMo_{11}VO_{40}$ was prepared according to the procedure reported in the literature [13,16]. Briefly, 15.8 g of MoO_3 and 0.91 g of V_2O_5 were added into 250 ml of deionized water and the resulting suspension was then heated up to the reflux temperature under stirring. Afterwards, 1.15 g of 85% (by mass) phosphoric acid solution was added into the above-prepared suspension. After 15 h of reflux with vigorous stirring, the insoluble oxides were dissolved and a deep-orange solution was formed. Finally, water in the solution was evaporated in a vacuum heater at 327 K and an orange solid was collected, into which a suitable amount of deionized water was added for the purification of $H_4PMo_{11}VO_{40}$ by recrystallization.

The cesium salts $Cs_xH_{4-x}PMo_{11}VO_{40}$ ($x = 2.5$ or 3.5) were prepared by the precipitation method reported by Okuhara [26]. An example for the preparation of $Cs_{2.5}H_{1.5}PMo_{11}VO_{40}$ was given as follows. 1.8 g of $H_4PMo_{11}VO_{40}$ was dissolved in 20 ml of deionized water at room temperature and then 3.0 ml of Cs_2CO_3 solution ($0.5\ mol\cdot L^{-1}$) was added slowly with vigorous stirring. By addition of the Cs_2CO_3 solution, the precipitate was formed. After being centrifuged and dried at 353 K, the obtained precipitate was calcined at 473 K for 3 h.

3-(1-Methylimidazolium-3-yl)propane-1-sulfonate (MIMPS) was prepared by following the procedure described by Leng *et al.* [29]. 1-Methylimidazole (9.02 g at 0.11 mol) and 1,3-propanesultone (12.21 g at 0.10 mol) were dissolved into 100 ml of toluene and then stirred at 323 K for 24 h under nitrogen atmosphere. A white precipitate (MIMPS) was formed and the solid was filtered and washed with ether three times, then dried at 373 K for 6 h under vacuum. The resulting MIMPS (0.31 g at 1.5 mmol) was added to the aqueous slurry of $Cs_{2.5}H_{1.5}PMo_{11}VO_{40}$ (2.1 g at 1.0 mmol) and followed by stirring the mixture at 353 K for 6 h. Water was removed by filtration to give the final product as the inorganic–organic dual modified catalyst $Cs_{2.5}(MIMPS)_{1.5}PMo_{11}VO_{40}$.

The MIMPS modified $H_4PMo_{11}VO_{40}$ catalyst was prepared by adding the designed amount of MIMPS to the aqueous solution of $H_4PMo_{11}VO_{40}$ and followed by stirring the mixture at room temperature for 24 h. Water in the solution was then evaporated in a vacuum heater at 327 K. The obtained solid was referred to as $(MIMPS)_{2.5}H_{1.5}PMo_{11}VO_{40}$.

2.3. Catalyst characterization

The infrared (IR) spectra of the prepared catalysts were collected on a Nicolet NEXUS 670 Fourier transform infrared spectrophotometer in KBr disks at room temperature. The ^{13}C NMR spectrum at 100.6 MHz was measured by a Bruker AVANCE III 400 WB spectrometer with a spinning rate of 6 kHz, a contact time of 1.75 ms, an interval of 2 s, an accumulation of 5000 times and hexamethylbenzene as an external standard of the chemical shift. Prior to the measurement, the sample was dried at 373 K overnight. The amounts of the Mo and V species in the catalysts before and after the reaction were measured by an IRIS Intrepid II XSP inductively coupling plasma-atomic emission spectrometer (ICP-AES). The elemental analysis (C, H, and N) was performed on a CHN elemental analyzer (Vario EL III). The amount of acidic protons in the catalysts was determined by acid–base titration [30,31]. The X-ray powder diffraction (XRD) patterns were obtained on a Philips PW3040/60 diffractometer using CuKα radiation ($\lambda = 0.1541$ nm) in a scanning range of 5–50° at a scanning rate of $1(°)\cdot min^{-1}$. The ESR spectra were recorded on a Bruker EMX-10/12 spectrometer at X-band at room temperature. The Brunner–Emmet–Teller (BET) surface areas of the samples were determined by the adsorption isotherms of N_2 at 77 K using a Micromeritics ASAP 2020 instrument. The samples were outgassed under vacuum at 423 K for 10 h prior to the adsorption measurements.

2.4. Catalytic hydroxylation of benzene

The hydroxylation of benzene was carried out in a two-necked 25 ml flask with a reflux condenser, which was placed in a thermostatic bath with a magnetic stirrer. In a typical catalytic reaction, the flask was charged with benzene (10 mmol), acetonitrile (6 ml) and catalyst (0.1 mmol) with vigorous stirring, and then heated to a reaction temperature of 338 K. The reaction was initiated by adding H_2O_2 solution (30%, by mass, 10 mmol) dropwise within 30 min. Afterwards, the mixture was further stirred at 338 K for 5 h. After the reaction was quenched, the reaction mixture was filtered and the collected solution was analyzed by a gas chromatograph (Agilent 6820) equipped with a flame ionization detector (FID) and a capillary column (DB-5, 30 m × 0.45 mm × 0.42 μm). The recovered solid catalyst was washed with acetone and dried under vacuum at 393 K and then reused in the next run. The concentration of H_2O_2 in its aqueous solution was determined iodometrically prior to use in the oxidation reaction. Self-decomposition of H_2O_2 as a function of time was monitored by measuring the volume of oxygen evolved.

3. Results and Discussion

3.1. Catalyst characterization

Fig. 1 shows the FT-IR spectra of MIMPS, $Cs_{2.5}H_{1.5}PMo_{11}VO_{40}$ and $Cs_{2.5}(MIMPS)_{1.5}PMo_{11}VO_{40}$. It can be seen that in the wavenumber region of 700–1100 cm^{-1}, $Cs_{2.5}H_{1.5}PMo_{11}VO_{40}$ represents the four featured peaks at 1060 ($P–O_a$), 962 ($Mo = O_d$), 865 ($Mo–O_b–Mo$) (corner-sharing) and 795 cm^{-1} ($Mo–O_c–Mo$) (edge-sharing), assigned to the Keggin structure of the HPA [11–13]. For $Cs_{2.5}(MIMPS)_{1.5}PMo_{11}VO_{40}$, the four peaks appear distinctively in spite of the slight shifts of their positions, indicating that the Keggin structure of heteropolyanion is well reserved after the protons in the HPA are substituted by MIMPS cations. Meanwhile, $Cs_{2.5}(MIMPS)_{1.5}PMo_{11}VO_{40}$ represents the new characteristic bands at 1572, 1193, and 653 cm^{-1}, attributed to C–N and S=O stretching, and C–H bending vibrations for the organic cations, respectively [32]. This clearly indicates that both organic and inorganic moieties in $Cs_{2.5}(MIMPS)_{1.5}PMo_{11}VO_{40}$ reserve the original structures of their parents. Additionally, the observed band shifts imply the formation of a new inorganic–organic HPA salt due to the electrostatic interactions between the organic cation and the