Short Communication

The hydroxylation of benzene to phenol over heteropolyacid encapsulated in silica

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ABSTRACT

The vanadium-substituted heteropoly acid ($H_5PMo_{10}V_2O_{40}$ nH_2O) (PMoV$_2$) was encapsulated in silica as an immobilized catalyst (PMoV$_2$@SiO$_2$) for the hydroxylation of benzene to phenol with H_2O_2. The PMoV$_2$@SiO$_2$ was prepared by the one-pot hydrolysis of tetraethyl orthosilicate (TEOS) with PMoV$_2$ and Pluronic P123, and then the P123 was removed by pyrolysis at 500 °C to give PMoV$_2$@SiO$_2$. The PMoV$_2$@SiO$_2$ was found to be highly porous with micropores, mesopores and macropores, and the PMoV$_2$@SiO$_2$ was highly active and selective for the hydroxylation of benzene under mild conditions. Moreover, the catalyst can be reused at least 5 times without obvious deactivation.

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1. Introduction

As an important intermediate for synthesizing phenol resins, caprolactam, fibers, and many other chemicals [1], phenol is industrially mainly produced by the three-step cumene process with high energy consumption, low yields (*ca.*5% based on the initial benzene), and environment pollution [2,3]. From the viewpoints of economy and the environment, the one-step hydroxylation of benzene to phenol is highly attractive [4] compared to the three-step cumene process and other methods for the produce of phenol, such as nucleophilic substitution of aryl halides and chlorination/sulfonation processes of benzene [5,6]. Recently, the oxidants for the direct hydroxylation of benzene to phenol have been investigated extensively, including nitrous oxide [7,8], hydrogen peroxide [4,9], molecular oxygen [2,10], as well as a mixture of oxygen and hydrogen [1]. Among these oxidants, hydrogen peroxide is a wise choice since it is cheap and efficient with nontoxic water as the only by-product.

Although the direct hydroxylation of benzene to phenol with hydrogen peroxide in liquid phase has been explored extensively, the process is associated with a poor selectivity, namely, a substantial overoxidation of phenol occurs, forming various by-products, such as catechol, hydroquinone, and benzoquinone [11]. The one-step hydroxylation of benzene to phenol with H_2O_2 is still an interesting topic, and efficient catalysts are the main research objectives. Transition metal catalysts have been developed for the oxidation of benzene with H_2O_2, including Ti, Fe, Cu and V [12–15], but the catalysts were limited in low selectivity

or bad reusability. Tanev *et al.* [4] Investigated the catalytic hydroxylation of benzene over Ti-MCM-41, which showed 68% conversion and 98% selectivity towards phenol under mild reaction conditions. Contrastingly, the conversion of benzene was about 31% with 95% selectivity to phenol over titanium silicalite-1 (TS-1) for the hydroxylation of benzene with hydrogen peroxide. Cu on MCM-41 was reported to be active for the hydroxylation of benzene, which gave 21% conversion of benzene and 94% selectivity to phenol [16]. Fe-MCM-41 was also found to be good catalyst for the hydroxylation of benzene to phenol [17]. In addition, V-containing catalysts were studied extensively since V was an active center for the hydroxylation of benzene to phenol under mild conditions. Vanadium oxide on clay was reported as catalyst for the hydroxylation of benzene to phenol with hydrogen peroxide by Xu *et al.* [18], and 14% conversion and 94% phenol selectivity were obtained. Vanadyl acetylacetonate complex grafted to periodic mesoporous organosilica was reported as a catalyst for the hydroxylation of benzene, which showed high selectivity towards the phenol and good recyclability [19]. Keggin type phosphovanadomolybdic acid supported on amine functionalized SBA-15 was developed and applied for the hydroxylation of benzene with 20% conversion of benzene and 95% selectivity towards phenol [20]. The drawback of the transition metal catalysts is the low selectivity, and the heteropolyacid catalysts were limited in the reusability. Thus the development of efficient and reusable catalysts is highly desirable for the hydroxylation of benzene to phenol.

Recently, immobilized heteropolyacid catalysts were developed and applied for related reactions, and thus the catalysts were recycled easily [21,22]. We had developed the polyoxometalate(POM)–ionic hybrid catalysts and used as efficient and reusable catalysts for the

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hydroxylation of benzene, which gave phenol in 31.4% with 95.8% selectivity [23]. Furthermore, the encapsulated heteropolyacid (HPA) $H_3PW_{12}O_{40}$ was reported to be highly active for the esterification [22]. And here, we developed a new strategy for synthesizing the V-containing catalyst $PMoV_2@SiO_2$ by hydrolyzation of tetraethyl orthosilicate (TEOS) with Keggin type $PMoV_2$ and nonionic (Pluronic P123). And then the precatalyst was pyrolyzed at 500 °C under Ar to give $PMoV_2@SiO_2$ catalyst. The catalyst $PMoV_2@SiO_2$ was characterized by Fourier transform infrared spectra (FT-IR), X-ray diffraction (XRD), and N_2 ad-desorption, and the $PMoV_2@SiO_2$ was found to be highly active, selective and reusable for the hydroxylation of benzene to phenol with hydrogen peroxide.

2. Results and discussions

2.1. Catalyst characterization

$PMoV_2@SiO_2$ was characterized by TF-IR, XRD and N_2 ad-desorption. As shown in Fig. S1(a), the FT-IR bands at 1060, 960, 860, and 780 cm^{-1} were assigned to $v_{as}(P−O)$, $v_{as}(Mo\!=\!O)$ (terminal oxygen), $v_{as}(Mo−O_b−Mo)$ (corner-sharping oxygen), and $v_{as}(Mo−O_c−Mo)$ (edge-sharping oxygen) for the Keggin structures of neat $PMoV_2$. The four Keggin-structured FT-IR bands were preserved for $PMoV_2@SiO_2$ with broader FT-IR peaks, and shifted to higher vibration frequencies with respect to $PMoV_2$. This comparison implies that Keggin structure $PMoV_2$ in $PMoV_2@SiO_2$ was preserved and the local environment of the Keggin unit is relatively affected by silica (siloxane and silanol groups) [22]. In order to find more insights into the catalyst, solid-state ^{31}P-NMR was performed for both $PMoV_2@SiO_2$ and $PMoV_2$ (see Fig. S2). A single peak at $−0.5$ ppm was observed for both $PMoV_2@SiO_2$ and $PMoV_2$, which implied that the keggin structure of the $PMoV_2$ remained well in $PMoV_2@SiO_2$. The N_2 adsorption–desorption isotherm is shown in Fig. S3. The catalyst $PMoV_2@SiO_2$ had a BET surface area of 177 m^{2}g^{-1}. As seen in Fig. S3(a), the steep rise at $P/P^o = 0$ indicated the existence of micropores, and the hysteresis loop in the P/P^o range from 0.45 to 1.0 reflects plenty of mesopores/macropores. The pore distribution was presented in Fig. S3(b), which showed irregular porous distribution with micro, meso and macropores. XRD patterns of $PMoV_2$ and $PMoV_2@SiO_2$ are shown in Fig. S4. Pure $PMoV_2$ presented a set of diffraction peaks for the triclinic crystal structure of the Keggin-type HPA. But no obvious peak was found in the catalyst $PMoV_2@SiO_2$, which indicates $PMoV_2$ was homogeneously disappeared in amorphous silica. Elemental analysis (EA) was used to analyze the composition of $PMoV_2@SiO_2$ and $PMoV_2@SiO_2$-Air, and the results are as followed ($PMoV_2@SiO_2$: found C 12.47 wt.%, H 1.496 wt.%; $PMoV_2@SiO_2$-Air: found C 0.13 wt.%, H 0.697 wt.%). From the EA results, we found the chemical difference (12.47 wt.% carbon contained in $PMoV_2@SiO_2$) between $PMoV_2@SiO_2$-Air with $PMoV_2@SiO_2$, and we can image that the $PMoV_2@SiO_2$ was covered with a thin C film from pyrolysis of P123, which was consistent with the literature results [24]. When the $PMoV_2@SiO_2$ was calcined again at 500 °C under air, the carbon film was combusted and the black $PMoV_2@SiO_2$ turn to light yellow solid $PMoV_2@SiO_2$-Air (Fig. S5). The content of vanadium in $PMoV_2@SiO_2$ is 0.0364 g V_2O_5/g (0.34 g $PMoV_2$/g) determined by ICP-AES.

2.2. The screening of the catalysts

Catalysts were tested for the hydroxylation of benzene with H_2O_2, and the results were showed in Table 1. We initially conducted the reaction without catalyst or with the V-free phosphomolybdic acid ($H_3PMo_{12}O_{40}$), and no phenol was obtained (entries 1, 2). The hydroxylation of benzene with homogeneous with single V-containing PMoV and double V-containing $PMoV_2$ gave phenol in 12.5% and 25.0% yield respectively (entries 3,4), which proved that the V is crucial and the double V-containing POM was more active for the hydroxylation of

benzene to phenol [25]. Similar yield (10.9% to 12.5%) of phenol was obtained by heterogeneous $PMoV@SiO_2$ catalyst compared to homogeneous PMoV (entry 5). In addition, the hydroxylation of benzene with $PMoV_2@SiO_2$ afforded phenol in high yield (21.6%) (entry 7). Interestingly, the catalyst $PMoV_2@SiO_2$-Air, which was calcined under air was not as active as $PMoV_2@SiO_2$, and phenol was obtained in 17.6% (entry 6). As $PMoV_2@SiO_2$ was covered with a thin carbon film, which may be helpful for the hydroxylation of benzene with H_2O_2. Additionally, activated carbon treated by H_2O_2 was reported to be active for the hydroxylation of benzene, which was consistent with the results [26].

2.3. Solvent effects

Solvents were tested for the hydroxylation of benzene, and the mixture of acetonitrile and acetic acid was suitable solvent. The effects of volume ratios of acetonitrile to acetic acid are summarized in Table 2. When pure acetonitrile and pure acetic acid were used as the solvent respectively, the yields of the phenol were low (16.7% and 16.1% respectively, Table 2, entries 1, 7). When mixture of acetonitrile and acetic acid was used as the solvent (volume ratio 5.5:0.5), the yield of phenol increased to 17.2% (Table 2, entry 2). The maximum yield of phenol was achieved in 21.6% with volume ratio of acetonitrile to acetic acid as 5:1 (Table 2, entry 3). The addition of more acetic acid led to decreasing yield of phenol (Table 2, entries 4–6). The addition of acidic acid can mix the two liquid phases (H_2O/CH_3CN) into one liquid phase, and then enhance the contact frequency of the reactants (benzene and H_2O_2). On the other hand, the yield of phenol is affected by the decomposition of H_2O_2. The weak acidic environment is beneficial for the hydroxylation of benzene [27]. However, the strong acidic environment can accelerate the decomposition of H_2O_2 [28], which leads to the decrease of phenol yield.

Table 1
The screening of catalysts for the hydroxylation of benzene to phenol with H_2O_2.[a]

Entry	Catalysts	Con.[b] (%)	Y.[c] (%)	Sel.[d] (%)
1	None	0	0	–
2	$H_3PMo_{12}O_{40}$	0	0	–
3[e]	PMoV	13.9	12.5	90[d]
4[f]	$PMoV_2$	26.3	25.0	95[d]
5	$PMoV@SiO_2$	11.8	10.9	92[d]
6	$PMoV_2@SiO_2$-Air	17.6	17.6	100
7	**$PMoV_2@SiO_2$**	**21.6**	**21.6**	**100**

Bold data indicates the highest yield among the catalysts.
[a] Reaction conditions: catalyst (150 mg, 0.06 mmol V), benzene (1 mL, 11.22 mmol), acetonitrile (5 mL), acetic acid (1 mL), H_2O_2 (30 wt.%, 3 mL, 29.5 mmol), 60 °C, 6 h; [b] Conversion of benzene; [c] Yield to phenol; [d] Selectivity for phenol, hydroquinone and benzoquinone as the by-products; [e] PMoV (100 mg, 0.06 mmol V); [f] $PMoV_2$ (50 mg, 0.06 mmol V).

Table 2
The optimization of the solvent mixture (volume ratio of acetonitrile to acetic acid) for the hydroxylation of benzene to phenol with H_2O_2.[a]

Entry	Acetonitrile/acetic acid	Con.[b] (%)	Y.[c] (%)	Sel. (%)
1	6/0	16.7	16.7	100
2	5.5/0.5	17.2	17.2	100
3	**5/1**	**21.6**	**21.6**	**100**
4	4.5/1.5	14.3	14.3	100
5	3/3	14.7	14.7	100
6	2:4	15.1	14.8	98[d]
7	0/6	16.1	15.3	95[d]

Bold data indicates the suitable volume ratio.
[a] Reaction conditions: benzene (1 mL, 11.22 mmol), solvent (6 mL), hydrogen peroxide (30 wt.%, 3 mL, 29.5 mmol), catalyst (150 mg, 0.06 mmol V), 60 °C, 6 h. [b] Conversion of benzene; [c] Yield to phenol; [d] Selectivity to phenol, hydroquinone and benzoquinone as the by-products.