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Direct hydroxylation of benzene with hydrogen peroxide over pyridine–heteropoly compounds

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ABSTRACT

The hybrid catalysts, pyridine (Py) modified molybdovanadophosphates with Keggin structure $Py_n–PMo_{(12-m)}V_mO_{40}$ ($n = 1–3$, $m = 1–3$), were prepared and characterized by FT-IR. Among various catalysts, $Py_1–PMo_{10}V_2O_{40}$ exhibited the highest yield of phenol (20.5%) with the selectivity of phenol of 98.0% at 353 K for 5 h in the direct hydroxylation of benzene to phenol with H_2O_2 in the acetic acid and acetonitrile (volume ratio 1:1) mixed solvent. Pyridine plays an important role in the promotion of the catalytic activities, mostly due to the electronic interaction between pyridine and heteropolyacid together with the more remarkable pseudo-liquid-phase behavior. The influences of the reaction temperature, the amount of H_2O_2, the amount of $Py_1–PMo_{10}V_2O_{40}$ and the reaction time on the yield of phenol were investigated to obtain the optimal reaction conditions for phenol formation.

1. Introduction

Phenol is industrially produced by a three-step cumene process, which gives low atom utilization, low phenol yield, high energy consumption, and the production of equal amount of acetone as the by-product [1]. Therefore, the one-step process of the direct hydroxylation of benzene into phenol has been attracting great interest for tens of years [2,3]. The synthesis of phenol from the direct hydroxylation of benzene can be achieved by various oxidants [4–10], including nitrous oxide [4], hydrogen peroxide [5], and molecular oxygen [6]. Hydrogen peroxide has been widely used as a green oxidant, because it is readily available and the resulting by-products (water and molecular oxygen) are environmentally friendly [11]. Moreover, various heterogeneous catalysts have been studied for this reaction [12–14], and the vanadium substituted heteropolyacid catalysts were revealed to be novel and efficient catalysts [15–17].

Heteropolyacids (HPAs) exhibit a wide range of molecular sizes, compositions and architectures, and have attracted much attention as catalysts because of their strong acidity and redox property, which can be controlled by replacing the protons with metal cations and/or by changing the heteroatom or the framework transition-metal atoms [18–20]. The Keggin-type HPAs with formula $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ have been used for various reactions [21–23]. In recent years, there has been an increasing interest in transition metal-substituted polyoxometalates (TMSPs) as catalysts for the oxidation of organic substrates, in which the substituted vanadium is known as the most active metal species for the hydroxylation of benzene [16,24,25]. Also, hybrid materials based on covalently linked polyoxometalates with organic species have been extensively studied by previous reports [26–28], which revealed a strong electronic interaction between the metal oxygen cluster and the organic segment in many of these hybrid materials. It was further proposed that the organic π electrons may extend their conjugation to the inorganic framework and thus dramatically modify the redox properties of the inorganic cluster [29–31]. Liu et al. used TMSP compounds $[(C_4H_9)_4N]_5[PW_{11}CuO_{39}(H_2O)]$ as the catalyst for the liquid-phase hydroxylation of benzene to phenol by molecular oxygen with ascorbic acid as a reducing agent in an acetone/sulfolane/water mixed solvent [32], and it showed 9.2% of benzene conversion (TON = 25.8) and 91.8% of selectivity of phenol at 323 K for 12 h. Wang et al. revealed that pyridine–heteropoly compounds were very active catalysts for phenol hydroxylation to dihydroxybenzenes with hydrogen peroxide as oxidant in aqueous solutions [33]. Therefore, the hybrid catalysts based on the combination of HPAs with an organic compound for the hydroxylation of benzene to phenol with hydrogen peroxide as oxidant are open to study.

In this work, vanadium-substituted HPAs (V-HPAs) were prepared and then transferred into their corresponding pyridinium salts to get hybrid materials. We apply them as catalysts for the liquid-phase hydroxylation of benzene with 30% H_2O_2, and observe

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a remarkable promotion effect of pyridine in the yield of phenol.

2. Experimental

2.1. Catalyst preparation and characterization

The purchased chemicals were in analytical grade and used without further purification. They are MoO_3, V_2O_5, H_3PO_4 (85%), $MeCO_2H$, benzene, phenol, benzoquinone (BQ), acetonitrile, acetic acid, H_2O_2 (30%), pyridine (Py) and $H_3PMo_{12}O_{40}{\cdot}23H_2O$ (PMo_{12}).

The procedure for the preparation of the vanadium-substituted heteropolymolybdic acid $H_4PMo_{11}VO_{40}$ is the following. 14.400 g MoO_3 and 0.910 g V_2O_5 were dissolved in 250 mL deionized water; then the solution was heated up to 393 K under vigorously stirring with a water-cooled condenser. 1.150 g H_3PO_4 (85% aqueous solution) was added to the above mixture with the temperature kept at 393 K. After stirred for 24 h, the product was cooled to room temperature and dried at 323 K in vacuum for 24 h. The resulting orange fine powder was then dissolved in deionized water and subjected to re-crystallization for further purification. The synthesis of $H_5PMo_{10}V_2O_{40}$ or $H_6PMo_9V_3O_{40}$ was similar to the above method with the difference that the content of the vanadium was corresponding to that of the target formula. Pyridine (Py) salts $Py_n{-}PMo_{(12-m)}V_mO_{40}$ (n = 1–3, m = 1–3) were prepared according to the methods reported by the previous literatures [34,35]. According to the different molar ratios of pyridine to $PMo_{(12-m)}V_mO_{40}$, a solution of pyridine in 30 mL aqueous solution was added dropwise into 20 mL aqueous solution of $PMo_{(12-m)}V_mO_{40}$ under stirring at room temperature. A white precipitate formed immediately. After stirred for 24 h, the resulting mixture was filtered and then dried in vacuum at 343 K for 24 h to produce the hybrid catalyst. The IR spectra of the catalysts were measured using a KBr disk mounted in an infrared spectrophotometer (Nexus 870).

2.2. Catalytic tests

The hydroxylation of benzene was carried out in a 50 mL three-necked round bottom flask equipped with a magnetic stirrer, a thermometer and a water-cooled condenser. In a typical reaction, the hybrid catalyst (0.200 g) and benzene (1.0 mL) were added to 25.0 mL of acetic acid and acetonitrile (volume ratio 1:1) mixed solvent. The resulting heterogeneous reaction system was vigorously stirred for 10 min after the temperature reached 353 K, then within 30 min, 3.5 mL of aqueous solution of 30% H_2O_2 was added dropwise into the mixture. After that, the solution was stirred for another 4.5 h at 353 K. The product mixture was analyzed by gas chromatography (SP-6890A) equipped with a FID detector and a capillary column (SE-54 30 m × 0.32 mm × 0.3 μm). An internal standard material 1,4-dioxane was used to the quantitatively analysis. Under the employed conditions, only benzoquinone was detected as the by-product. Yield of phenol (or benzoquinone) = mmol phenol (or benzoquinone)/mmol initial benzene. Selectivity of phenol = mmol phenol/(mmol phenol + mmol benzoquinone). Selective conversion of H_2O_2 = (mmol phenol + mmol 2benzoquinone)/mmol initial H_2O_2.

3. Results and discussion

3.1. IR results

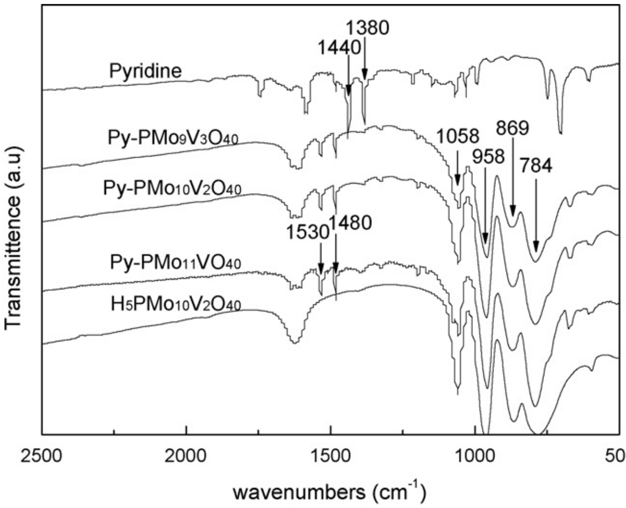

Fig. 1. FT-IR spectra of pyridine, $H_5PMo_{10}V_2O_{40}$ and $Py_1{-}PMo_{(12-m)}V_m$ (m = 13).

The IR spectra of pyridine, $H_5PMo_{10}V_2O_{40}$ and $Py_1{-}PMo_{(12-m)}V_m$ (m = 1–3) are illustrated in Fig. 1. It can be seen that $H_5PMo_{10}V_2O_{40}$ and $Py_1{-}PMo_{(12-m)}V_mO_{40}$ (m = 1–3) showed all the four IR vibration peaks assigned to a Keggin-structured heteropolyacid, and the locations of featured peaks (P–O, 1058 cm^{-1}; Mo–O–Mo, 958 cm^{-1}; Mo–O, 869 cm^{-1} and 784 cm^{-1}) were in well agreement with those in the previous report [36]. This indicates that the Keggin structure for the prepared samples is well retained after the proton in HPAs is exchanged by pyridinium ion. The IR spectra of $Py_1{-}PMo_{(12-m)}V_mO_{40}$ (m = 1–3) also showed a clear shift of the featured bands for pyridinium ions from 1440 cm^{-1} and 1380 cm^{-1} to 1530 cm^{-1} and 1480 cm^{-1}, respectively, which was in agreement with the previous research [37]. Maybe these shifts can be explained by the extended conjugation of π electrons of Py into the inorganic framework of HPA [31], i.e., a strong electronic interaction between the metal oxygen cluster in heteropoly anions and the Py segment can be proposed by the IR results.

3.2. Effect of pyridine in hybrid catalysts on the hydroxylation of benzene

Table 1 shows the results of the hydroxylation of benzene with hydrogen peroxide over different catalysts. It can be seen that no phenol was detected over the vanadium-free $H_3PMo_{12}O_{40}$ catalyst. For comparison, the experiment using pure V_2O_5 as the catalyst was carried out under the same conditions, and V_2O_5 proved to be active in this reaction with a low phenol yield of 7.5%. By substituting molybdenum by vanadium, $H_5PMo_{10}V_2O_{40}$ exhibited a doubly enhanced yield of phenol of 15.4% with a lowered selectivity of

Table 1
Catalytic performance of different catalysts in the hydroxylation of benzene with hydrogen peroxide[a]

Catalyst	Y_{phenol}[b] (%)	$Y_{benzoquinone}$[c] (%)	S_{phenol}[d] (%)	$X_{H_2O_2}$[e] (%)
$H_3PMo_{12}O_{40}$	0	0	–	–
V_2O_5	7.5	0	100	2.5
$H_5PMo_{10}V_2O_{40}$	15.4	1.0	93.9	5.8
Pyridine	0	0	–	–
$Py_1{-}PMo_{10}V_2O_{40}$	20.5	0.4	98.0	7.1

[a] Reaction conditions: 0.200 g catalyst; 1.0 mL (11.28 mmol) benzene; 3.5 mL (33.95 mmol) 30% H_2O_2; 25.0 mL solvent (acetic acid:acetonitrile = 1:1); 353 K reaction temperature; 5 h reaction time.

[b] Yield of phenol.

[c] Yield of benzoquinone.

[d] Selectivity of phenol.

[e] Selective conversion of H_2O_2.

Table 2
Effect of the amount of pyridine in the hybrid catalysts $Py_n–PMo_{(12-m)}V_mO_{40}$ (m = 1–3, n = 1–3) for the hydroxylation of benzene with hydrogen peroxide at 353 K[a]

Catalyst	Y_{phenol}[b] (%)	$Y_{benzoquinone}$[c] (%)	S_{phenol}[d] (%)	$X_{H_2O_2}$[e] (%)
$H_4PMo_{11}V_1O_{40}$	7.8	0.2	97.5	2.7
$Py_1–PMo_{11}V_1O_{40}$	9.4	0.2	97.9	3.2
$Py_2–PMo_{11}V_1O_{40}$	8.4	0.3	96.6	3.0
$Py_3–PMo_{11}V_1O_{40}$	6.1	0.2	96.8	2.2
$Py_1–PMo_{10}V_2O_{40}$	20.5	0.4	98.0	7.1
$Py_2–PMo_{10}V_2O_{40}$	16.2	0.5	97.0	5.7
$Py_3–PMo_{10}V_2O_{40}$	10.8	0.3	97.3	3.8
$H_6PMo_9V_3O_{40}$	13.8	0.5	96.5	4.9
$Py_1–PMo_9V_3O_{40}$	14.7	0.3	98.0	5.1
$Py_2–PMo_9V_3O_{40}$	15.6	0.2	98.7	5.3
$Py_3–PMo_9V_3O_{40}$	12.4	0.1	99.2	4.2

[a] Reaction conditions: 0.200 g catalyst; 1.0 mL (11.28 mmol) benzene; 3.5 mL (33.95 mmol) 30% H_2O_2; 25.0 mL solvent (acetic acid:acetonitrile = 1:1); 5 h reaction time.

[b] Yield of phenol.

[c] Yield of benzoquinone.

[d] Selectivity of phenol.

[e] Selective conversion of H_2O_2.

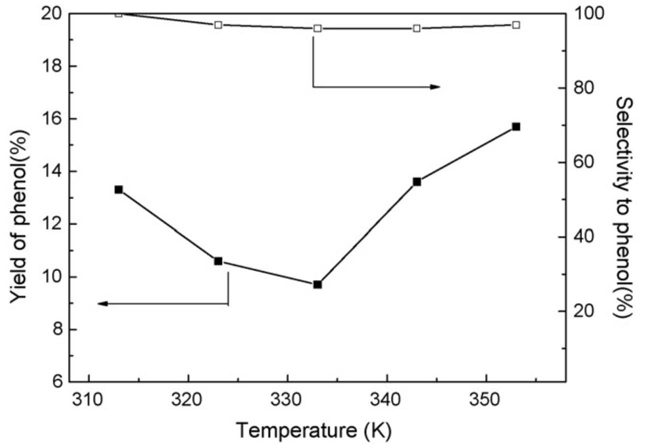

Fig. 2. Effect of reaction temperature on the yield and selectivity to phenol in hydroxylation of benzene over the $Py_1–PMo_{10}V_2O_{40}$ catalyst.

phenol of 93.9%. Clearly, the presence of vanadium atoms in heteropolyacid is essential for efficiently performing the hydroxylation of benzene to phenol. It is suggested that the catalysis by HPAs for the hydroxylation of benzene is due to the cooperative action of the molybdenum framework with one vanadium center [17]. It is noteworthy that, although pyridine itself was not active in the reaction, the formation of the heteropolyacid salt $Py_1–PMo_{10}V_2O_{40}$ by combining pyridine with $H_5PMo_{10}V_2O_{40}$ resulted in a further increase of the yield of phenol from 15.4% to 20.5% and an increased selectivity from 93.9% to 98.0%. This indicates an obvious promotion effect of pyridine on the hydroxylation of benzene to phenol. However, only a very low effective conversion of hydrogen peroxide was obtained even on the $Py_1–PMo_{10}V_2O_{40}$ catalyst.

In order to investigate the effect of pyridine, the activities of catalysts at various molar ratios of pyridine to $PMo_{(12-m)}V_mO_{40}$ (m = 1–3) were compared. The results are listed in Table 2. It is seen that in addition to $H_5PMo_{10}V_2O_{40}$, for $H_4PMo_{11}V_1O_{40}$ and $H_6PMo_9V_3O_{40}$ the introducing of pyridine into the catalysts also led to the increase of yield of phenol, i.e., the promotion effect of pyridine is also true for $Py_n–PMo_9V_3O_{40}$ and $Py_n–PMo_{11}V_1O_{40}$ (n = 1–3). At the same molar ratio of pyridine to $PMo_{(12-m)}V_mO_{40}$ (m = 1–3), the catalytic activities of $Py_n–PMo_{10}V_2O_{40}$ were higher than that of $Py_n–PMo_{11}V_1O_{40}$ and $Py_n–PMo_9V_3O_{40}$ (n = 1–3). This is in accordance with our previous result over the Py-free molybdovanadophosphoric acid catalysts [15].

Molar ratio of pyridine to $PMo_{(12-m)}V_mO_{40}$ (m = 1–3) is also responsible for the reactivity of hydroxylation of benzene. Table 2 showed that at a given number of m (m = 1, 2, or 3), the yield of phenol generally decreased with the increase of molar ratio of pyridine to $PMo_{(12-m)}V_mO_{40}$. When the molar ratio of pyridine to $PMo_{(12-m)}V_mO_{40}$ (m = 1, 2, or 3) was 1 or 2, the catalytic activities of $PMo_{(12-m)}V_mO_{40}$ were more or less promoted by pyridine, but the further increase of the ratio up to 3 resulted in a substantial decrease of the catalytic activities, which were lower than the corresponding Py-free catalysts. It is known that for organic compound modified hybrid HPA catalysts, there exists a strong electronic interaction between the metal oxygen cluster and the organic segment, and it is proposed that the organic π electrons may extend their conjugation to the inorganic framework and thus dramatically modify the redox properties of the cluster [29–31]. IR spectra in Fig. 1 also suggest this interaction for the present catalysts. In addition, it was previously reported that the pyridine molecules can be adsorbed not only on the surface acid sites, but also on the acid sites located in the bulk of HPA crystals, thereby expanding the lattice spacing between the polyanions in the crystal [38]. Thus, the pseudo-liquid-phase behavior of heteropolyacid is more remarkable, and it is more beneficial for organic reactant benzene to enter the bulk of polyanions. For these reasons, the combination of pyridine with HPA catalysts promotes the catalytic activities for the benzene hydroxylation, just as indicated in Tables 1 and 2. However, pyridine is a weak base that is able to largely adjust the acidity of HPAs if too many pyridines were introduced in the hybrid catalysts [33], which may reversely result in a lowered yield of phenol, as in case of $Py_3–PMo_{(12-m)}V_mO_{40}$ (m = 1–3).

3.3. *Effect of reaction conditions on the hydroxylation of benzene*

The influence of reaction temperature on the reactivity of hydroxylation of benzene was investigated using $Py_1–PMo_{10}V_2O_{40}$ as the catalyst, and the results are illustrated in Fig. 2. At temperatures below 333 K, the yield of phenol decreased with increasing the reaction temperature, and at temperature above 333 K, it increased with the reaction temperature. At very low reaction temperature of 313 K, only phenol was detected as the product, and at increased temperatures, a slight of benzoquinone was observed. We have confirmed this trend by repeatedly carrying out this test.

According to the Arrhenius Equation, the reaction rate should always increase with the increase of reaction temperature if the catalytic reaction takes place on a certain active site. Therefore, the reasonable explanation for the phenomenon in Fig. 2 should ascribe to a change of active species upon the increase of reaction temperature. A number of previous reports investigating the stability of V-HPA as the catalyst for the hydroxylation of benzene [16,24,25,39–42] explicitly revealed that the vanadic oxide species might segregate from the structures of heteropolyanions. They observed the difference of ^{51}V NMR, ^{31}P NMR and FT-IR spectra for the catalysts before and after use in the reaction and suggested the existence of cationic VO_2^+ species that was responsible for the deactivation of recovered V-HPA for phenol formation. It was proposed that the leached cationic VO_2^+ species must be generated from the somewhat decomposition of HPA, despite that the Keggin structure of HPA was well remained. Based on those previous findings, in Fig. 2, one can thus deduce that the increased reaction temperature may cause the extraction of more amounts of vanadic oxide species from the hybrid V-HPA catalyst, and the enhanced activity due to the increasing of the reaction temperature cannot compensate the lowered activity due to the existence of segregated

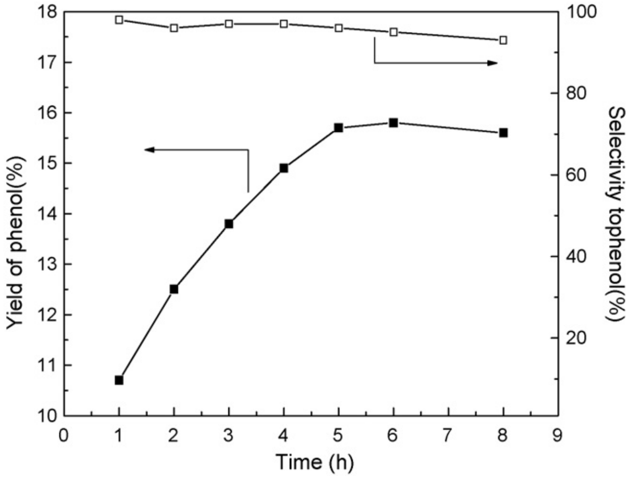

Fig. 3. Effect of reaction time on the yield and selectivity to phenol in hydroxylation of benzene over the Py_1–$PMo_{10}V_2O_{40}$ catalyst.

vanadic oxide species. 353 K is considered as a suitable reaction temperature.

Fig. 3 shows the result for the hydroxylation of phenol as a function of reaction time over Py_1–$PMo_{10}V_2O_{40}$ catalyst at a reaction temperature of 353 K. It can be observed that the yield of phenol increased smoothly with the reaction time up to 5 h and then stayed at a constant level. The selectivity of phenol decreased slightly with the reaction time, which is due to the further oxidation of phenol. This indicates that the optimum reaction time is 5 h.

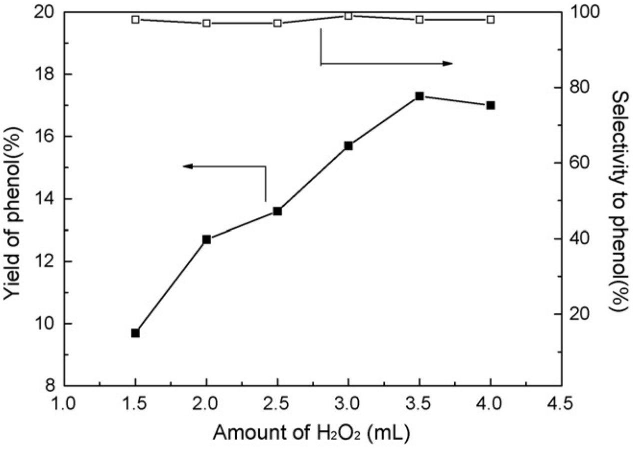

Fig. 4. Effect of amount of H_2O_2 on the yield and selectivity to phenol in hydroxylation of benzene over the Py_1–$PMo_{10}V_2O_{40}$ catalyst.

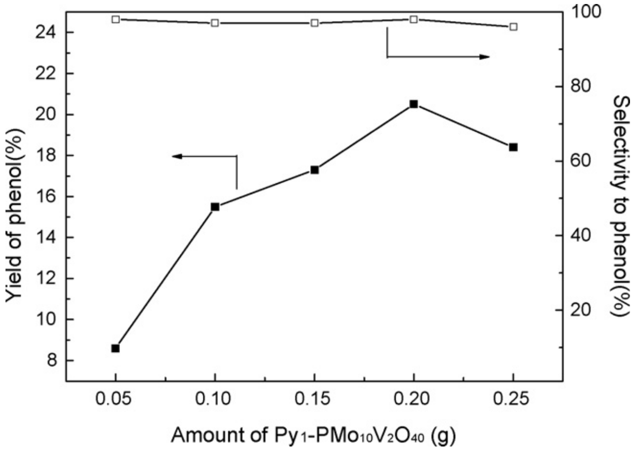

Fig. 5. Effect of the amount of the catalyst on the yield and selectivity to phenol in hydroxylation of benzene over the Py_1–$PMo_{10}V_2O_{40}$ catalyst.

The influence of the amount of H_2O_2 on the yield and the selectivity of phenol over Py_1–$PMo_{10}V_2O_{40}$ is listed in Fig. 4. It is seen that the yield of phenol was positively dependent on the amount of H_2O_2 and reached a maximum value of 17.3% at 3.5 mL (at this moment, the molar ratio of hydrogen peroxide to benzene is equal to 3). A slight decrease in the yield of phenol was observed with a further increase the amount of H_2O_2, which may result from the further oxidation of the phenol formed. The selectivity of phenol did not show a remarkable change as the amount of H_2O_2 increased. Theoretically, the molar ratio of H_2O_2 to benzene for the hydroxylation reaction is 1:1; however, the results suggest that the H_2O_2 needed for the favorable phenol yield was about three times as high as its stoichiometry. In fact, the self-decomposition of H_2O_2 is unavoidable accompanying with the hydroxylation of benzene. We thus carried out a H_2O_2 self-decomposition experiment at typical reaction conditions mentioned in experimental section without involving benzene and catalyst (i.e., only with solvent), and after the reaction, the H_2O_2 concentration in solvent was determined by the titration with sodium thiosulfate (starch as indicator) in the presence of potassium iodide, sulfuric acid and ammonium molybdate. The amount of H_2O_2 consumed in its self-decomposition was 20.65 mmol, accounting for 60.8% of the initial H_2O_2. This may provide some understandings for the very low selective conversion of H_2O_2 shown in Tables 1 and 2.

Fig. 5 displays the effect of the amount of Py_1–$PMo_{10}V_2O_{40}$ on the yield and the selectivity of phenol in the reaction. It can be seen that the yield of phenol increased from 8.6% to 20.5% when the amount of Py_1–$PMo_{10}V_2O_{40}$ increased from 0.050 g to 0.200 g. A further increase in the amount of Py_1–$PMo_{10}V_2O_{40}$ caused a decrease in the yield of phenol, and the selectivity of phenol kept constant. Thus, 0.200 g Py_1–$PMo_{10}V_2O_{40}$ is a suitable amount in this reaction.

4. Conclusions

In this work, we prepared the pyridine modified molybdovanadophosphate hybrid catalysts for the direct hydroxylation of benzene by hydrogen peroxide in the acetic acid and acetonitrile mixed solvent, and find they show both high yield and high selectivity of phenol. The substituted vanadium atoms in heteropolyacid are essentially active sites with high performance for the hydroxylation of benzene to phenol. More importantly, pyridine can promote substantially the catalytic activities of the hybrid catalysts due to the electronic interaction between pyridine and heteropolyacid together with the more remarkable pseudo-liquid-phase behavior. In particular, Py_1–$PMo_{10}V_2O_{40}$ exhibits the highest activity for the hydroxylation of benzene with 98.0% selectivity of phenol and 20.5% phenol yield at the optimum reactions conditions: 1.0 mL benzene, 3.5 mL 30% aqueous solution of H_2O_2, 0.200 g catalyst, 25 mL acetic acid and acetonitrile (volume ratio 1:1) mixed solvent, 353 K reaction temperature, and 5 h reaction time.

Acknowledgements

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