

Pyridine- $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ hybrid catalysts for liquid-phase hydroxylation of benzene to phenol with molecular oxygen

GE HanQing¹, LENG Yan¹, ZHANG FuMin¹, PIAO JiaRui², ZHOU ChangJiang¹ & WANG Jun^{1†}¹ State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, China;² Petrochemical Research Institute, PetroChina Company Ltd., Beijing 100083, China

Pyridine(Py)-modified Keggin-type vanadium-substituted heteropoly acids ($\text{Py}_n\text{PMo}_{10}\text{V}_2\text{O}_{40}$, $n=1$ to 5) were prepared by a precipitation method as organic/inorganic hybrid catalysts for direct hydroxylation of benzene to phenol in a pressured batch reactor and their structures were detected by FT-IR. Among various catalysts, $\text{Py}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}$ exhibits the highest catalytic activity (yield of phenol, 11.5%), without observing the formation of catechol, hydroquinone and benzoquinone in the reaction with 80 vol% aqueous acetic acid, molecular oxygen and ascorbic acid used as the solvent, oxidant and reducing reagent, respectively. Influences of reaction temperature, reaction time, oxygen pressure, amount of ascorbic acid and catalyst on yield of phenol were investigated to obtain the optimal reaction conditions for phenol formation. Pyridine can greatly promote the catalytic activity of the Py-free catalyst ($\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$), mostly because the organic π electrons in the hybrid catalyst may extend their conjugation to the inorganic framework of heteropoly acid and dramatically modify the redox properties, at the same time, pyridine adsorbed on heteropoly acids can promote the effect of “pseudo-liquid phase”, thus accounting for the enhancement of phenol yield.

hydroxylation, benzene, organic/inorganic hybrid catalyst, phenol, heteropoly acid, pyridine

1 Introduction

Phenol is an important intermediate for the manufacture of petrochemicals, agrochemicals and plastics. More attention has been paid to searching a new process to produce phenol without by-products, with a high selectivity and under mildest conditions in order to replace the existing three-step cumene process^[1]. The direct hydroxylation of benzene to phenol can be achieved by various oxidants; molecular oxygen is a better choice in industrial applications based on the economical and environmental considerations^[2–8].

Keggin-type heteropoly acids have many advantages making them economically and environmentally attractive in both academic and industrial context. They are acidic and redox catalysts for various reactions since

their strong acidity and redox property can be controlled by replacing the protons with metal cations and/or by changing the heteroatom or the framework transition-metal atoms^[9–11]. The additional interesting aspects of polyoxometalates (POMs) in catalysis are their inherent stability towards oxygen donors such as molecular oxygen and hydrogen peroxide. Therefore, POMs are useful catalysts for liquid-phase oxidation of hydrocarbons. In recent years, there has been an increasing interest in transition metal-substituted polyoxometalates

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†Corresponding author (email: junwang@njut.edu.cn)

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(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^[12,13]. Liu et al. used TMSP compounds [(C₄H₉)₄N]₅[PW₁₁CuO₃₉(H₂O)] 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, showing 9.2% of benzene conversion and 91.8% of selectivity to phenol at 323 K for 12 h^[14]. On the other hand, organic/inorganic hybrid materials are extremely interesting as catalytic materials^[15–17]. For hybrid materials composed by POMs and organic species, the close interaction of organic delocalized *p* electrons with the inorganic *d* electrons may bring about exciting synergistic effects^[18]. In redox reactions, this interaction may dramatically modify the redox properties of the cluster^[19,20].

We consider that the secondary structure of the heteropoly acid manifests itself to exhibit extremely high proton mobility and “pseudo-liquid phase” behavior^[21–23] that can be easily utilized in the design of catalysts. In such cases, not only water but also a variety of polar organic molecules can enter and leave the interpolyanion space in the structure and react there. Therefore, in this work, the organic/inorganic hybrid materials, i.e. the pyridine-modified vanadium-substituted heteropoly acids, are prepared as the catalysts for the liquid-phase hydroxylation of benzene with molecular oxygen as the oxidant. An obvious promotion effect of pyridine in the hybrid catalysts on the phenol yield is observed for this reaction.

2 Experimental

2.1 Preparation of catalysts

All solvents and reagents were purchased commercially and used without further purification.

Keggin-type vanadium-substituted heteropolymolybdic acid (H₅PMo₁₀V₂O₄₀·*x*H₂O) was prepared at the P/Mo/V molar ratio of 1:10:2 using MoO₃, V₂O₅, and aqueous 85% H₃PO₄ as reactants^[24]. The detail of the preparation procedure is as follows: MoO₃ (14.39 g, corresponding to 100 mmol MoO₃) (Shanghai Chem. Reagent Co., AR) and V₂O₅ (1.82 g, corresponding to 10 mmol V₂O₅) (Shanghai Chem. Reagent Co., AR) were suspended in 150 mL de-ionic water in a 500-mL three-necked flask equipped with a condenser and magnetic stirring in an oil bath at the reflux temperature.

Aqueous 85% H₃PO₄ (1.15 g, or 10 mmol H₃PO₄, Shanghai Chem. Reagent Co., AR) was added dropwise to the boiling and stirred suspension of the reaction mixture. The above mixture was kept at 393 K and stirred for 24 h, and then a clear orange-red solution was obtained. The solution was cooled to room temperature and was further dried *via* evaporation to get a solid product, into which a suitable amount of de-ionic water was added to obtain a solution, and then the solution was left at room temperature overnight to re-crystallize for purification. The resulting fine orange-red powders were characterized and used later for hydroxylation of benzene.

Pyridine-modified molybdovanadophosphoric acid denoted by Py_{*n*}PMo₁₀V₂O₄₀ was prepared by a precipitation method. For example, Py₁PMo₁₀V₂O₄₀ was prepared by adding the specified amount of H₅PMo₁₀V₂O₄₀ into 25 mL aqueous solution containing pyridine (Shanghai Chem. Reagent Co., AR) with the pyridine/H₅PMo₁₀V₂O₄₀ molar ratio of 1 : 1. And then the solution containing precipitates was dried *via* evaporation at 343 K. The solid product obtained was further dried at 343 K for 12 h in a vacuum oven.

2.2 Liquid-phase hydroxylation of benzene

The liquid-phase hydroxylation of benzene was carried out in a custom-designed temperature controllable titanic reactor (100 mL) with a mechanical stirrer.

The typical reaction conditions are as follows: 0.10 g catalyst, 0.60 g ascorbic acid (Shanghai Chem. Reagent Co., AR), 25.0 mL of 80 vol% aqueous acetic acid, and 2.0 mL of benzene (Shanghai Chem. Reagent Co., AR) were added into the reactor. When the reactor was heated to the desired temperature, oxygen was injected into the reactor up to the preset pressure. The hydroxylation was conducted for 10 h with stirring. After the reaction, 1.0 mL 1,4-dioxane (Shanghai Chem. Reagent Co., AR) was added into the reaction mixture as an internal standard for product analysis.

Measurements of gas chromatography (GC, SP-6890A) equipped with an FID detector and a capillary column (SE-54; 30 m×0.32 mm×0.25 μm) were performed to analyze the product mixture. Phenol was the only product detected by GC, and no catechol, hydroquinone and benzoquinone were observed.

2.3 Measurement of the IR spectra of catalysts

IR spectra of the catalysts were measured using a KBr disk mounted in an infrared spectrophotometer. Samples

were mixed and ground with KBr for IR measurement.

3 Results and discussion

3.1 Catalyst characterization

IR spectra of pyridine, $\text{Py}_n\text{PMo}_{10}\text{V}_2\text{O}_{40}$ ($n=1-5$) and $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ are illustrated in Figure 1. It can be seen that $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ and $\text{Py}_n\text{PMo}_{10}\text{V}_2\text{O}_{40}$ ($n=1-5$) gave all the IR vibration peaks assigned to a Keggin-type heteropoly acid, and the locations of featured peaks (PsO, 1057 cm^{-1} ; MosOsMo, 958 cm^{-1} ; ModO, 865 and 785 cm^{-1}) are in good agreement with those in the previous report^[24]. This indicates that the Keggin structure for prepared samples is well retained after the proton in heteropoly acid is replaced by pyridinium ion. The prepared $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ was orange-red in color, and easily soluble in water, and took on a blue color upon treatment with a mild reducing agent (i.e. ascorbic acid), which qualitatively supports the conclusion that the prepared vanadium-substituted heteropoly acid possesses the Keggin-type HPA structure. From 1600 to 1200 cm^{-1} , the IR spectrum of pyridine clearly showed two peaks at 1439 and 1385 cm^{-1} (curve A in Figure 1). After the reaction of pyridine with $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$, the two corresponding peaks respectively shifted to 1535 and 1483 cm^{-1} (curves B, C, D, E and F in Figure 1), which is in agreement with the previous research^[25].

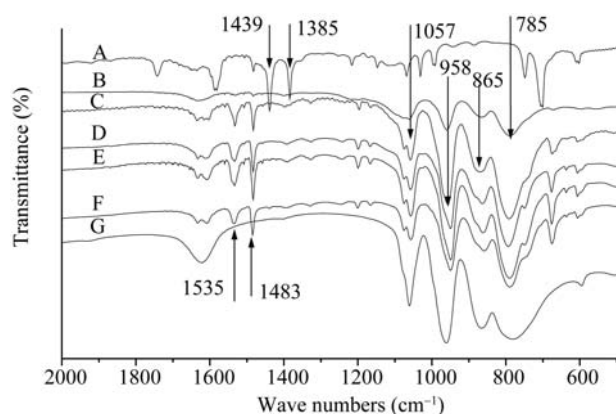


Figure 1 FT-IR spectra of various catalysts. A: Pyridine; B: $\text{Py}_1\text{PMo}_{10}\text{V}_2\text{O}_{40}$, C: $\text{Py}_2\text{PMo}_{10}\text{V}_2\text{O}_{40}$, D: $\text{Py}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}$, E: $\text{Py}_4\text{PMo}_{10}\text{V}_2\text{O}_{40}$, F: $\text{Py}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$, G: $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$.

The above phenomena are known to be related to pyridine adsorbed on Brønsted acid sites and Lewis acid sites, which were generated by the formation of pyridinium ions in the bulk, as well as the formation of

the primary oxygen-deficient Keggin structure^[26]. The Lewis acid sites around the oxygen-deficient Keggin surface structure seem to be created by the removed lattice oxygen during the reaction of heteropoly acid with pyridine at the evaporation pretreatment. Because there is a strong electronic interaction between the metal oxygen cluster and the organic segment^[20,27], it is obvious that the strength of metal-O bond becomes weaker due to the increase of the electronic density of Keggin units by the incorporated pyridine. Tani et al. investigated the reaction mechanism of hydroxylation of benzene to phenol catalyzed by vanadium-substituted heteropoly acid with molecular oxygen through isotope labeling, and found that O_2 was activated on the partially reduced vanadium-substituted heteropoly acid and that the activated oxygen reacted with benzene to eventually form phenol^[6]. So the strong electronic effect between pyridine and $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ may possibly enhance remarkably the catalytic activity of pyridine-modified vanadium-substituted heteropoly acids.

3.2 Evaluation of catalytic performances of various catalysts

The catalytic activities of $\text{Py}_n\text{PMo}_{10}\text{V}_2\text{O}_{40}$ ($n=1-5$) and $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ in the direct hydroxylation of benzene to phenol with molecular oxygen at 373 K are shown in Table 1. It can be seen that no phenol was detected without using ascorbic acid as reducing reagent. When ascorbic acid was added into the reaction mixture without catalyst, only 1.4% yield of phenol was achieved. Under the employed conditions, $\text{Py}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}$ exhibited the highest catalytic activity among those catalysts. No other product than phenol was detected by GC analysis in all entries. By introducing pyridine into the heteropoly acid, the catalytic activity was substantially

Table 1 Direct hydroxylation of benzene to phenol at 373 K over various catalysts^{a)}

Catalyst	Yield of phenol (%) ^{b)}
No catalyst without ascorbic acid	not detected
No catalyst with ascorbic acid	1.4
$\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$	3.9
$\text{PyPMo}_{10}\text{V}_2\text{O}_{40}$	5.4
$\text{Py}_2\text{PMo}_{10}\text{V}_2\text{O}_{40}$	10.5
$\text{Py}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}$	11.5
$\text{Py}_4\text{PMo}_{10}\text{V}_2\text{O}_{40}$	5.9
$\text{Py}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$	5.8

a) Reaction conditions: 0.10 g catalyst, 0.60 g ascorbic acid, 2.0 mL benzene, 25.0 mL aqueous solution containing 80 vol% acetic acid, 2.0 MPa oxygen, 373 K , 10 h; b) yield of phenol (%) = mmol phenol/mmol initial benzene.

improved, maybe due to the strong electronic interaction between Keggin units and pyridine^[20,27]. Figure 1 suggests that the organic π electrons may extend their conjugation to the inorganic framework, which would weaken the strength of metal-O bond, and thus the catalytic activity would be promoted.

Additionally, as is well known, not only water but also a variety of polar organic molecules can enter and leave the interpolyanion space in the structure and react there^[22,23]. When pyridine was adsorbed on the surface of Keggin units, it would help benzene enter the bulk of Keggin units easily and contact the catalytic center. However, pyridine is a weak base being able to largely adjust the acidity of heteropoly acids if too much pyridine was introduced in the hybrid catalyst^[28], which may reversely result in the lowered yield of phenol. As shown in Table 1, the yield of phenol was the highest at 11.5% when the ratio of pyridine to $\text{PMo}_{10}\text{V}_2\text{O}_{40}$ unit was 3. Synergistic effect produced by the electronic interaction and the “pseudo-liquid phase” property may account for the improvement of the catalytic activity. By contrast, Yamaguchi et al.^[29] reported the hydroxylation of benzene to phenol catalyzed by $\text{Cs}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ with molecular oxygen as the oxidant. Under their reaction conditions (0.02 mmol catalyst, 5.6 mmol benzene, 5 mL HAc (80 vol%), 1 mmol ascorbic acid, 0.4 MPa O_2 , 353 K, 24 h), the yield of phenol was only 7.2%.

3.3 Effect of reaction temperature on yield of phenol

The effect of the reaction temperature on the yield of phenol over $\text{Py}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}$ is shown in Figure 2. 373 K was considered as the suitable reaction temperature. This is probably due to the excessive oxidation of the product (phenol) at high temperatures, leading to the lower value of the phenol yield. Coke is the most possible deep oxidation product, because catechol, hydroquinone and benzoquinone were not detected by GC.

3.4 Effect of oxygen pressure on yield of phenol

The influence of the oxygen pressure on the yield of phenol was investigated using $\text{Py}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}$ as the catalyst, and the results are illustrated in Figure 3. The phenol yield was found to be the maximum at 11.5% when the oxygen pressure was increased to 2.0 MPa. As is well known, the solubility of oxygen in water, in general, increases with increase of the pressure of oxygen, but too much oxygen may cause the excessive oxidation of the produced phenol. Therefore, 2.0 MPa was the suitable reaction pressure.

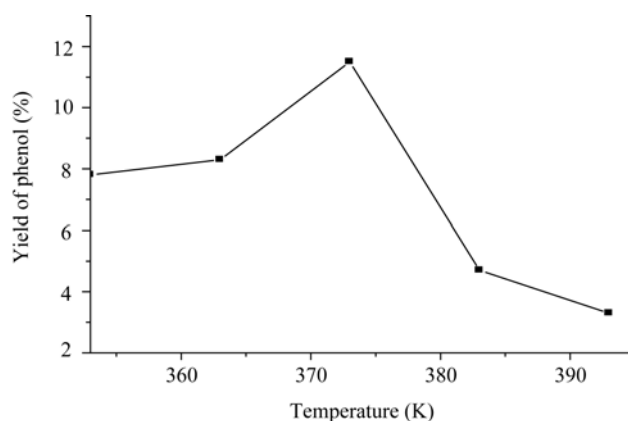


Figure 2 Effect of reaction temperature on the phenol yield over $\text{Py}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}$ catalyst. Reaction conditions: 0.10 g catalyst, 0.60 g ascorbic acid, 2.0 mL benzene, 25.0 mL aqueous solution containing 80 vol% acetic acid, 2 MPa oxygen, 10 h.

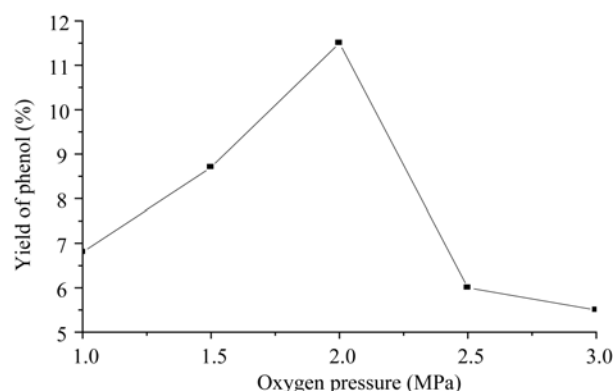


Figure 3 Effect of oxygen pressure on phenol yield over $\text{Py}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}$ catalyst. Reaction conditions: 0.10 g catalyst, 0.60 g ascorbic acid, 2.0 mL benzene, 25.0 mL aqueous solution containing 80 vol% acetic acid, 373 K, 10 h.

3.5 Effect of amount of ascorbic acid on yield of phenol

The results of the effect of the amount of ascorbic acid on the yield of phenol investigated at 373 K over $\text{Py}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}$ are shown in Figure 4. When the amount of ascorbic acid increased from 0.10 to 0.40 g, the yield of phenol increased slowly, and then greatly increased up to 11.5% when the amount of ascorbic acid was up to 0.60 g, but a further increase in the amount of ascorbic acid caused a sharp decrease. The role of the reducing reagent was suggested to activate the oxygen molecule through the reduction of the V species. However, excessive ascorbic acid may decrease sharply the activated oxygen species which are necessary for phenol formation so that almost no activated oxygen species can be utilized for the benzene oxidation^[30]. Therefore,

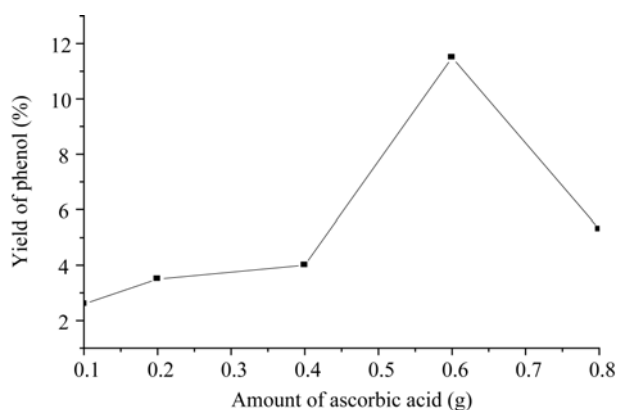


Figure 4 Effect of amount of ascorbic acid on phenol yield over $\text{Py}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}$ catalyst. Reaction conditions: 0.10 g catalyst, 2.0 mL benzene, 25.0 mL aqueous solution containing 80 vol% acetic acid, 373 K, 2 MPa, 10 h.

0.60 g ascorbic acid was considered as a suitable amount in this reaction.

3.6 Effect of amount of $\text{Py}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}$ on yield of phenol

As shown in Figure 5, when the amount of $\text{Py}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}$ increased from 0.05 g to 0.10 g, the yield of phenol increased sharply from 4.6% to 11.5%. On the other hand, a further increase in the amount of $\text{Py}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}$ caused a sharp decrease in the yield of phenol (from 11.5% for 0.10 g to 1.7% for 0.80 g). This may be due to the deep oxidation of benzene and/or the produced phenol by the excessive catalyst.

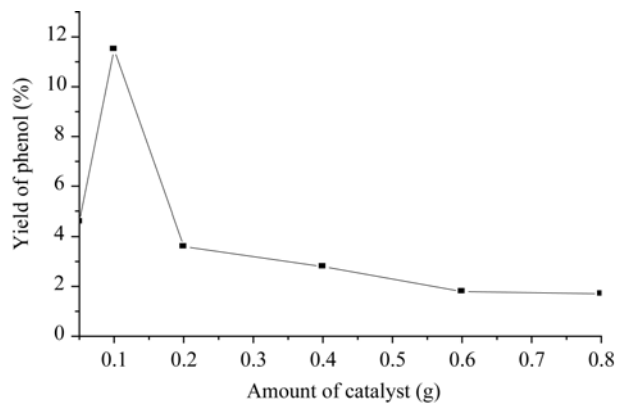


Figure 5 Effect of amount of $\text{Py}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}$ catalyst on the phenol yield. Reaction conditions: 0.60 g ascorbic acid, 2.0 mL benzene, 25.0 mL aqueous solution containing 80 vol% acetic acid, 373 K, 2 MPa, 10 h.

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3.7 Effect of reaction time on yield of phenol

The influence of reaction time on the yield of phenol over $\text{Py}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}$ is shown in Figure 6. It is obvious that the yield of phenol reached the maximized 11.5% when the reaction time was 10 h. After that, the yield decreased sharply due to further oxidation of the product (phenol).

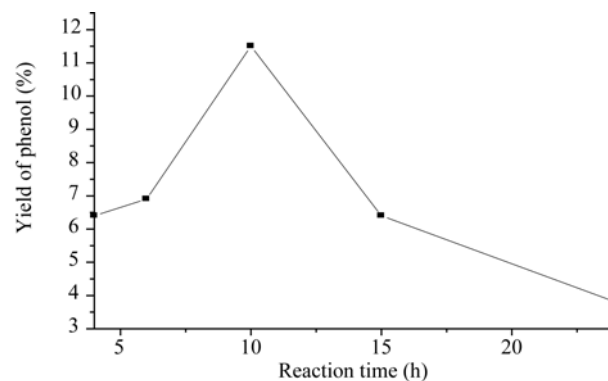


Figure 6 Effect of the reaction time on the phenol yield over $\text{Py}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}$ catalyst. Reaction conditions: 0.10 g catalyst, 0.60 g ascorbic acid, 2.0 mL benzene, 25.0 mL aqueous solution containing 80 vol% acetic acid, 373 K, 2 MPa.

4 Conclusions

Organic/inorganic hybrid catalyst $\text{Py}_n\text{PMo}_{10}\text{V}_2\text{O}_{40}$ can be easily prepared with $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ and pyridine by the precipitation method and its Keggin-type structure is kept well. $\text{Py}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}$ is demonstrated to be a good catalyst in the direct hydroxylation of benzene to phenol with molecular oxygen and ascorbic acid as the oxidant and the reducing reagent, respectively. The highest yield of phenol, 11.5%, is achieved in a batch reactor under the optional reaction conditions: 0.10 g catalyst, 0.6 g ascorbic acid, 2.0 mL benzene, 25.0 mL aqueous solution containing 80 vol% acetic acid, 373 K, oxygen pressure of 2.0 MPa, and 10 h. Pyridine plays an important role in the reaction for the improvement of the catalytic activity because of the strong electronic effect between pyridine and $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ together with the “pseudo-liquid phase” property. However, the excessive amounts of pyridine and catalyst, and longer reaction time have disadvantageous effects on the yield of phenol.

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