

Direct Hydroxylation of Benzene to Phenol with Molecular Oxygen over Phase Transfer Catalysts: Cyclodextrins Complexes with Vanadium-Substituted Heteropoly Acids

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Abstract Cyclodextrins (CyDs) complexes with vanadium-substituted heteropoly acids ($\text{PMoV}_n\text{-}\beta\text{-CyDs}$, $n = 1, 2$) were prepared by simple mixing and their structures were characterized by FT-IR. Among various catalysts, $\text{PMoV}_1\text{-}\beta\text{-CyDs}$, an efficient phase transfer catalyst, exhibited the highest yield (13.1%) of phenol without observing the formation of catechol, hydroquinone and benzoquinone in direct hydroxylation of benzene to phenol in 80 vol% aqueous acetic acid with molecular oxygen and ascorbic acid used as the oxidant and the reducing reagent, respectively. The influences of the reaction temperature, the pressure of oxygen, the amount of ascorbic acid, the amount of catalyst, and the reaction time on the yield of phenol were investigated to obtain the optimal reaction conditions for phenol formation.

Keywords Hydroxylation of benzene · Phase transfer catalysis · Phenol · Vanadium-substituted heteropoly acid · Cyclodextrins

1 Introduction

Phenol is an important intermediate for the manufacture of petrochemicals, agrochemicals and plastics [1–3]. It is mainly produced by cumene process. However, this process consists of three steps, and has many disadvantages. For example, the yield of phenol remains only 5%, accompanied by great energy consumption especially in

the distillation process for separation among the products and the reactants [4]. Hence, finding a one-step process for the production of phenol by direct hydroxylation of benzene attracts much attention in recent years [5–11].

The direct synthesis of phenol from benzene and nitrous oxide, a very toxic and global-warming related gas molecule, has been described [12], but this method is only cost-effective when nitrous oxide is available cheaply as a by-product [13]. Therefore, there is a need for the search of new processes to produce phenol without by-products, with a high selectivity and at the reaction conditions as mild as possible. Bahidsky et al. reported the gas phase hydroxylation of benzene to phenol catalyzed by the Cu-modified phosphate catalysts in the presence of oxygen and ammonia at 723 K and a very poor yield of phenol was obtained [14]. Lemke et al. investigated the direct hydroxylation of benzene to phenol by hydrogen peroxide on vanadium oxide catalysts supported on MCM-41, MCM-48, silica of Aerosil type and AMM [3]. Low to moderate yield of phenol and selectivity were achieved. As has been recently shown, active peroxide-type species can be obtained by an in situ reductive activation of molecular oxygen when a catalytic oxidation of hydrocarbons is conducted in the presence of co-reductants [2, 15–18]. Tsuruya and co-workers [19–21] reported the use of molecular oxygen as the oxidant for the one-step oxidation of benzene to phenol using Cu-ZSM-5 as a catalyst. Only 4.9% of the yield with ca. 30% selectivity was achieved at their optional reaction conditions. In 2007, Kubacka et al. developed the Cu ion-exchanged ZSM-5 system for the one-step formation of phenol by direct oxidation of benzene, in presence of molecular oxygen as well as an oxygen/hydrogen mixture [8]. They found that the yield of phenol increased with temperature up to 673 K and approached a high value of ca. 10%. Glacial acetic acid

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was employed as the solvent for the first time in the direct hydroxylation of benzene to phenol at room temperature using vanadium-substituted heteropolyacids and hydrogen peroxide as the catalysts and the oxidant, respectively [22]. A yield of 26% was achieved with a selectivity of 91%.

Catalytic function of polyoxometalates has attracted much attention because their acidic and redox properties can be controlled at atomic and molecular levels. The strong acidity and oxidizing property of polyoxometalates attract a lot of studies on the heterogeneous and homogeneous catalysis [23–31]. The additional interesting aspects of polyoxometalates in catalysis are their inherent stability towards oxygen donors such as molecular oxygen and hydrogen peroxide. Therefore, polyoxometalates are useful catalysts for liquid-phase oxidation of hydrocarbons.

We have attempted the liquid-phase oxidation of benzene to phenol catalyzed by vanadium-substituted heteropoly acids using H_2O_2 as the oxidant [32]. In extending the study of liquid-phase benzene oxidation, this paper reports the catalytic behaviors of the cyclodextrins (CyDs) complexes with vanadium-substituted heteropoly acids ($\text{PMoV}_n\text{-}\beta\text{-CyDs}$, $n = 1, 2$) for the liquid-phase hydroxylation of benzene under the various reaction conditions, with molecular oxygen and ascorbic acid used as the oxidant and the reducing reagent, respectively.

2 Experimental

2.1 Preparation of Catalysts

All solvents and reagents were purchased from commercial sources and used without further purification.

Keggin-type molybdovanadophosphoric acids ($\text{H}_{3+n}\text{PMo}_{12-n}\text{V}_n \cdot x\text{H}_2\text{O}$) were prepared at the P/Mo/V ratio of 1:(12 - n): n ($n = 1, 2$) using MoO_3 , V_2O_5 , and aqueous 85% H_3PO_4 as reactants [33]. For example, $\text{H}_4\text{PMo}_{11}\text{V}$ was prepared as follows: MoO_3 (18.580 g, corresponding to 11.73 mmol Mo_{11}) (Shanghai Chem. Reagent Co., AR) and V_2O_5 (1.067 g, corresponding to 11.73 mmol V) (Shanghai Chem. Reagent Co., AR) were suspended in 150 mL de-ionic water in a 500-mL three-necked flask equipped with a condenser under magnetic stirring in an oil bath at the reflux temperature. Aqueous 85% H_3PO_4 (Shanghai Chem. Reagent Co., AR) was added drop-wise to the boiling and stirred suspension of the metal oxides. After the addition of the phosphoric acid, a clear orange-red solution was obtained. The solution 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 as the control catalyst in the hydroxylation of benzene.

The cyclodextrins (CyDs) complexes with vanadium-substituted heteropoly acids ($\text{PMoV}_n\text{-}\beta\text{-CyDs}$, $n = 1, 2$) were prepared by adding the specified amount of HPMoV_n into 25 mL of a hot aqueous β -cyclodextrins (Shanghai Chem. Reagent Co., AR) solution to form the $\beta\text{-CyDs/PMoV}_n$ molar ratio of 1:1. The precipitates obtained ($\text{PMoV}_n\text{-}\beta\text{-CyDs}$, $n = 1, 2$) were dried at 343 K overnight in vacuum oven and used as the catalyst in the hydroxylation of benzene.

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 were as follows: 0.100 g catalyst and 0.400 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 in turn carefully. When the reactor was subjected to the desired temperatures, oxygen was injected into the reactor up to the preset pressure. The hydroxylation was conducted for 10 h under stirring. After the reaction, 1.0 mL of 1,4-dioxane (Shanghai Chem. Reagent Co., AR), which was confirmed as unchanged during the treatment, was added into the reaction mixture as an internal standard for product analysis. The final product mixture after reaction and prior to the GC analysis was observed to be in the homogenous state.

Gas chromatographic (GC) measurements were performed on a SP-6890A equipped with a FID detector and a capillary column (SE-54; 30 m \times 0.32 mm \times 0.25 μm). This reaction system appeared to have a high selectivity since phenol was the only product detected by GC. Among all catalysts, phenol was produced as the only reaction product without observing the formation of catechol, hydroquinone and benzoquinone.

2.3 Measurement of the IR Spectra of the Catalysts

The IR spectra of the catalysts were measured using a KBr disk mounted in an infrared spectrophotometer (Nexus 870). Samples were mixed and grounded with KBr for IR measurement.

3 Results and Discussion

3.1 Catalyst Characterization

The IR spectra of PMoV_n , $\text{PMoV}_n\text{-}\beta\text{-CyDs}$ ($n = 1, 2$) and $\beta\text{-CyDs}$ are illustrated in Fig. 1. From Fig. 1, it can be seen

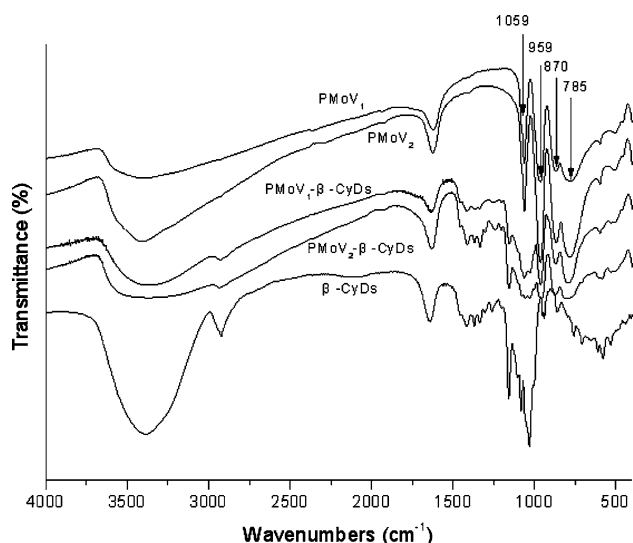


Fig 1 FT-IR spectra of various catalysts

that PMoV_n and $\text{PMoV}_n\text{-}\beta\text{-CyDs}$ ($n = 1, 2$) in this work showed all the IR vibration peaks assigned to a Keggin-type heteropolyacid, and the locations of featured peaks (PsO , $1,059\text{ cm}^{-1}$; MosOsMo , 959 cm^{-1} ; ModO , $870, 785\text{ cm}^{-1}$) are in well agreement with those in the previous report [33]. The prepared PMoV_n ($n = 1, 2$) catalysts were orange-red in color, very soluble in water, and took on a blue color upon treatment with a mild reducing reagent, such as ascorbic acid. These results also provided qualitative support for the conclusion that the prepared vanadium-substituted heteropoly acids have Keggin-type HPA structures.

The IR spectra of $\text{PMoV}_n\text{-}\beta\text{-CyDs}$ ($n = 1, 2$) and $\beta\text{-CyDs}$ from $1,200$ to $1,500\text{ cm}^{-1}$ are very similar to each other and the OH group peaks of $\text{PMoV}_n\text{-}\beta\text{-CyDs}$ ($n = 1, 2$) are obviously weaker than that of $\beta\text{-CyDs}$, which showed that PMoV_n ($n = 1, 2$) have been interacted with $\beta\text{-CyDs}$ possibly via the hydrogen bond and retain their Keggin-type structures well.

3.2 Evaluation of Performances of Various Catalysts

The catalytic activity of PMoV_n and $\text{PMoV}_n\text{-}\beta\text{-CyDs}$ ($n = 1, 2$) in the direct hydroxylation of benzene to phenol with molecular oxygen at 383 K is shown in Table 1. It can be seen that no phenol was detected without ascorbic acid used as the reducing reagent. When ascorbic acid was added into the reaction mixture without a catalyst, only 1.7% yield of phenol was achieved. Under the working conditions, PMoV_1 and PMoV_2 displayed the same catalytic activity. $\text{PMoV}_1\text{-}\beta\text{-CyDs}$ exhibited the highest catalytic activity among those catalysts. No other products were detected by GC analysis in all entries. $\beta\text{-CyDs}$ can obviously improve the catalytic activity (3.0% for PMoV_1 vs. 5.2% for $\text{PMoV}_1\text{-}\beta\text{-CyDs}$, 3.0% for PMoV_2 vs. 3.3%

Table 1 Direct hydroxylation of benzene at 383 K over various catalysts^a

Catalyst	Yield of phenol (%) ^b
No catalyst ^c	— ^d
No catalyst	1.7
PMoV_1	3.0
PMoV_2	3.0
$\text{PMoV}_1\text{-}\beta\text{-CyDs}$	5.2
$\text{PMoV}_2\text{-}\beta\text{-CyDs}$	3.3

^a Reaction conditions: 0.100 g catalyst, 0.400 g ascorbic acid, 2.0 mL benzene, 25.0 mL of an aqueous solution containing 80 vol% acetic acid, 2.0 MPa oxygen, 383 K , 10 h

^b Yield of phenol (%) = mmol phenol/mmol initial benzene

^c No ascorbic acid

^d Means not detected

for $\text{PMoV}_2\text{-}\beta\text{-CyDs}$, respectively), which maybe owe to the unique cavity of $\beta\text{-CyDs}$. The cavity of $\beta\text{-CyDs}$ is apolar, and thus any reactions, which proceed rapidly in apolar media, should be accelerated simply by a “microsolvent effect” [34]. As is well known, the solubility of apolar guest compounds in water is in general increased when they forms inclusion complexes with $\beta\text{-CyDs}$. Thus, $\beta\text{-CyDs}$ is a potent phase-transfer catalyst [35].

As suggested in Fig. 2, the hydrophobic substrate (S) benzene in the organic phase enters the cavity of $\beta\text{-CyDs}$ and contacts the catalytic center PMoV_1 . After the reaction, the product (P) phenol is released into the aqueous phase at the liquid/liquid interface and the transfer cycle can go on [36]. What’s more, the product can be rapidly released from the catalytic center and avoid to be oxidized further, which may account for the result that only phenol was detected as the product over all of the $\beta\text{-CyDs}$ complexes in the direct hydroxylation of benzene.

3.3 Effect of the Reaction Temperature on the Yield of Phenol

The effect of the reaction temperature on the yield of phenol over $\text{PMoV}_1\text{-}\beta\text{-CyDs}$ is shown in Fig. 3. The yield

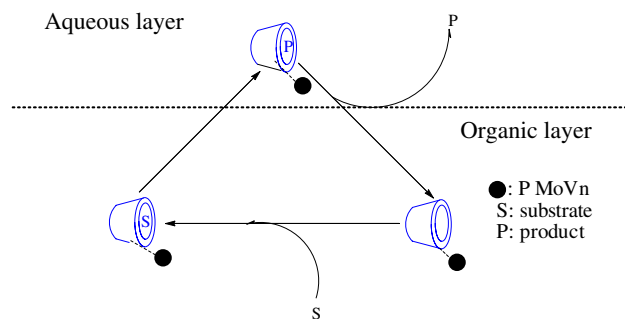


Fig. 2 Mechanism of phase transfer catalysis by $\beta\text{-CyDs}$ complexes

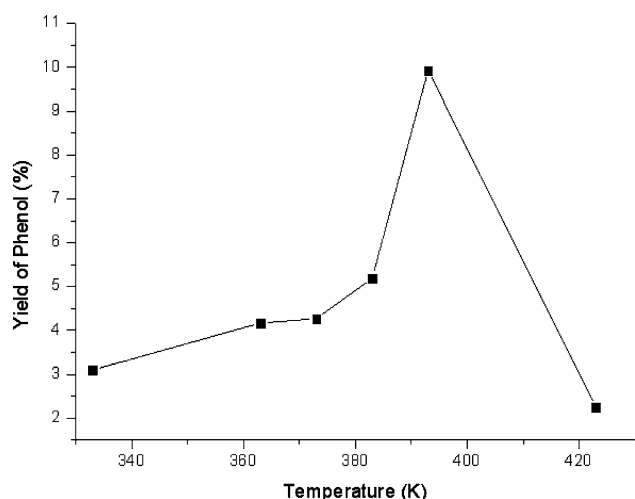


Fig. 3 The effect of phenol yield on the reaction temperature over $\text{PMoV}_{1-\beta}\text{-CyDs}$. Reaction conditions: 0.100 g catalyst, 0.400 g ascorbic acid, 2.0 mL benzene, 25.0 mL of an aqueous solution containing 80 vol% acetic acid, 2.0 MPa oxygen, 10 h

increased slowly from 3.1% to 5.2% when the reaction temperature was enhanced from 333 to 383 K, and then sharply raised up to 9.9% when the temperature reached to 393 K. However, when the reaction temperature was further up to 423 K, the yield of phenol sharply dropped to 2.3%. This is mostly caused by the excessive oxidation of the product (phenol), and these deep oxidized products could not be well determined by GC analysis. Therefore, 393 K was considered as a suitable reaction temperature.

3.4 Effect of the Oxygen Pressure on the Yield of Phenol

The yield of phenol as functions of the oxygen pressure is illustrated in Fig. 4. The phenol yield was found to increase with the increase of the oxygen pressure up to 1.5 MPa where it reached to ca. 13.1%. Further increase of oxygen pressure had a reverse influence on the phenol yield, which quickly decreased to 1.9%. 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 product (phenol). Therefore, 1.5 MPa is considered as a suitable reaction pressure.

3.5 Effect of the Amount of Ascorbic Acid on the Yield of Phenol

The results for the effect of the amount of ascorbic acid on the yield of phenol investigated at 393 K over $\text{PMoV}_{1-\beta}\text{-CyDs}$ are shown in Fig. 5. Almost no product was produced when no ascorbic acid was present as the reducing reagent. The yield of phenol increased with increasing

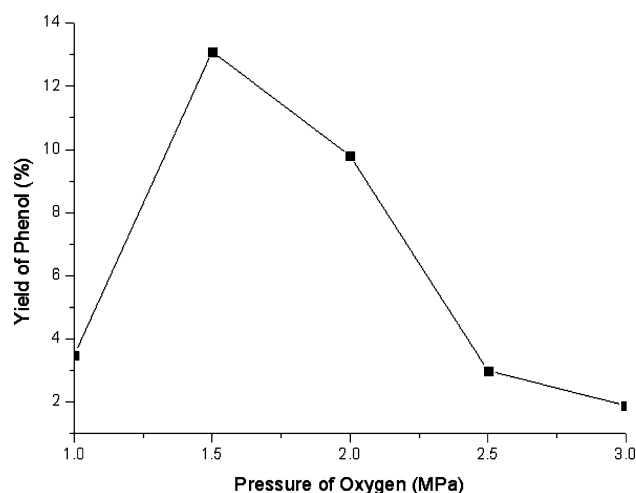


Fig. 4 The effect of the oxygen pressure on phenol yield over $\text{PMoV}_{1-\beta}\text{-CyDs}$. Reaction conditions: 0.100 g catalyst, 0.400 g ascorbic acid, 2.0 mL benzene, 25.0 mL of an aqueous solution containing 80 vol% acetic acid, 393 K, 10 h

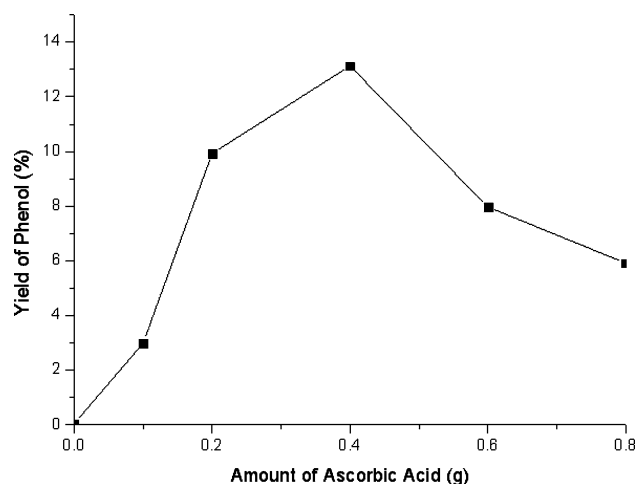


Fig. 5 The effect of the amount of ascorbic acid on phenol yield over $\text{PMoV}_{1-\beta}\text{-CyDs}$. Reaction conditions: 0.100 g catalyst, 2.0 mL benzene, 25.0 mL of an aqueous solution containing 80 vol% acetic acid, 393 K, 1.5 MPa, 10 h

amount of ascorbic acid up to 0.400 g, but a further increase in the amount of ascorbic acid inversely caused a decrease in the yield of phenol. The role of the reducing reagent was suggested to activate the oxygen molecule through the reduction of the V species, however, an extra ascorbic acid may decrease the activated oxygen species as well as [37]. The yield of phenol had a maximum value at the amount of ascorbic acid of around 0.400 g. The activated oxygen species are necessary for phenol formation, without utilizing for the benzene oxidation and thus the extra ascorbic acid is not in favor of the increase in phenol yield. Therefore, 0.400 g ascorbic acid was considered as a suitable amount in this reaction.

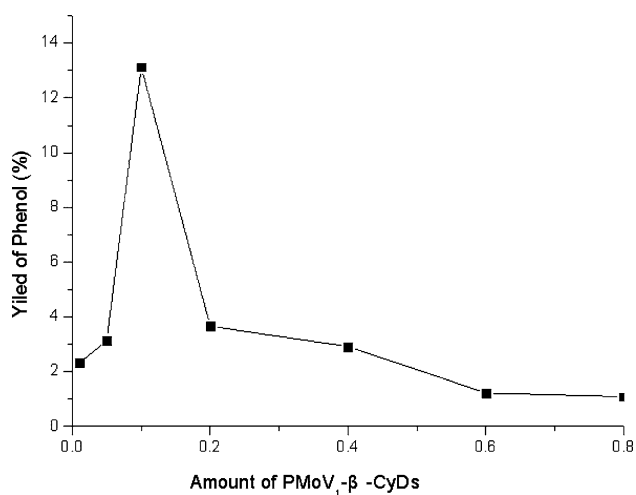


Fig. 6 The effect of the amount of PMoV₁-β-CyDs on the yield of phenol. Reaction conditions: 0.400 g ascorbic acid, 2.0 mL benzene, 25.0 mL of an aqueous solution containing 80 vol% acetic acid, 393 K, 1.5 MPa, 10 h

3.6 Effect of the Amount of PMoV₁-β-CyDs on the Yield of Phenol

As shown in Fig. 6, when the amount of PMoV₁-β-CyDs increased from 0.010 to 0.100 g, the yield of phenol increased sharply from 2.3% to 13.1%. When the amount of PMoV₁-β-CyDs increased from 0.100 to 0.200 g, the yield of phenol decreased sharply from 13.1% to 3.7%. On the other hand, a further increase in the amount of PMoV₁-β-CyDs caused a slight decrease in the yield of phenol (from 3.7% for 0.200 g to 1.1% for 0.800 g). As is well known, benzene and phenol can be completely oxidized by containing vanadium catalysts [38–40]. The reason causing the decrease of the yield of phenol with the increase of the

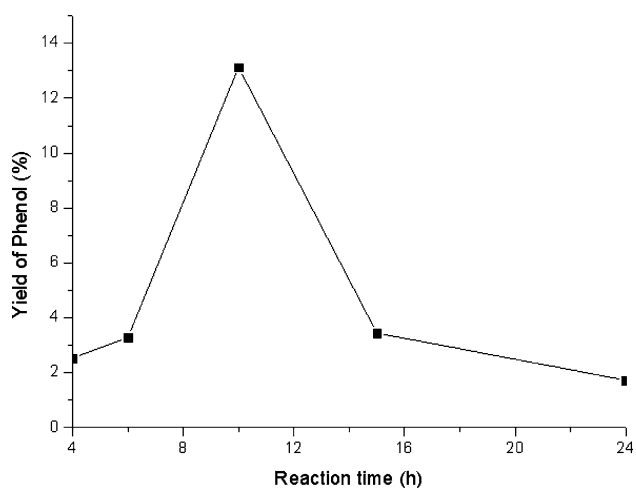


Fig. 7 The effect of the reaction time on the yield of phenol. Reaction conditions: 0.100 g catalyst, 0.400 g ascorbic acid, 2.0 mL benzene, 25.0 mL of an aqueous solution containing 80 vol% acetic acid, 393 K, 1.5 MPa

catalyst may be benzene and (or) the product (phenol) were deep oxidized by the extra catalyst. So, 0.100 g PMoV₁-β-CyDs was chosen as a suitable amount in this reaction.

3.7 Effect of the Reaction Time on the Yield of Phenol

The influence of reaction time on the yield of phenol over PMoV₁-β-CyDs is shown in Fig. 7. It is obvious that the yield of phenol increased greatly with the increase of reaction time up to 10 h, and after that, the yield decreased sharply with the increase of reaction time. The sharply decrease of yield may be caused by the further oxidation of the product (phenol), so 10 h was chosen as a suitable reaction time in this work.

4 Conclusions

PMoV_n can easily be interacted with the β-CyDs and their Keggin-type structures remained well. PMoV₁-β-CyDs is demonstrated to be a good phase-transfer catalyst in the direct hydroxylation of benzene to phenol with molecular oxygen as the oxidant. The highest yield of phenol, 13.1%, is achieved in a batch reactor under optional reaction conditions: 0.100 g catalyst, 0.400 g ascorbic acid, 2.0 mL benzene, 25.0 mL of an aqueous solution containing 80 vol% acetic acid, 393 K, 1.5 MPa, and 10 h.

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