

Direct synthesis of phenol from benzene catalyzed by multi-V-POMs complex

Hua Yang^{a,b,c}, Qing Wu^d, Jun Li^{a,b}, Wen Dai^{a,b,c}, Hengyun Zhang^{a,b}, Dan Lu^e, Shuang Gao^{a,b,*}, Wansheng You^{d,**}

^a Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences, Dalian 116023, PR China

^b Dalian National Laboratory for Clean Energy (DNL), Dalian 116023, PR China

^c University of Chinese Academy of Sciences, Beijing 100049, PR China

^d Institute of Chemistry for Functionalized Materials, Liaoning Normal University, 850 Huanghe Road, Dalian 116029, PR China

^e Liren College of Yanshan University, Qinhuangdao 066004, PR China

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ABSTRACT

A novel catalyst, [Mo₂V₂O₉(bpy)₆][PMo₁₁VO₄₀], was synthesized by the self-assembling of [PMo₁₁VO₄₀]⁴⁻ and [Mo₂V₂O₉(bpy)₆]⁴⁺ unit and characterized by elemental analyses, TG, IR, X-ray powder diffraction and X-ray single crystal diffraction. [Mo₂V₂O₉(bpy)₆][PMo₁₁VO₄₀] with multi-isolated active sites showed good catalytic activities for hydroxylation of benzene to phenol. A high yield of phenol (25.5%) with selectivity to phenol of 90.7% was obtained using H₂O₂ as oxidant. The catalyst can be recycled for 5 times while its structure was unchanged and its catalytic activity was maintained.

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1. Introduction

Phenol is widely used as an important chemical intermediate [1]. Industrially, 93% phenol production all over the world has been produced by three step cumene process. The cumene process produces a potential hazard cumyl hydroperoxide intermediate [2], a co-product acetone and needs a large amount of inorganic acid that brings up great pressures on the environment. The overall phenol yield of cumene process was no more than 5% (based on the initial benzene). A lot of efforts have been made to develop new techniques to solve these drawbacks, direct synthesis of phenol from benzene is preferred. With regard to the low phenol yields and low selectivities to phenol (due to the fact that benzene is hard to be oxidized and phenol is easily suffered from over oxidation) [3], a series of well performed catalysts for hydroxylation of benzene have been designed and synthesized [4–17].

POMs (polyoxometalates) were one kind of good oxidative catalyst owing to their stable structures and excellent oxidation resistance. Their catalytic activities can be finely manipulated because various early transition metals can be introduced into their structures at molecular levels [9–21]. Different early transition metals substituted POMs showed different activities in the synthesis of phenol from benzene [17]. Among them, vanadium-substituted POMs (for example, PMoV) showed good performance in the hydroxylation of benzene to phenol and aroused many studies [9–17]. Multi vanadium have been introduced into POMs in order to improve their catalytic activities, but the yields of phenol achieved by the three catalysts were decreased as follows: H₄[PMo₁₁VO₄₀] > H₅[PMo₁₀V₂O₄₀] > H₆[PMo₉V₃O₄₀] [9], which may be caused by the accumulation of disordered vanadium active sites in POMs.

There is a strategy to increase the vanadium content simultaneously avoiding vanadium accumulation in POMs anions: using vanadium-containing cations instead of their usual counter ions (H⁺, Na⁺, K⁺). In our previous work [22], a quadracationic [Mo₂V₂O₉(bpy)₆]⁴⁺ was found matched well with several POMs. In this contribution, the well performed [PMo₁₁VO₄₀]⁴⁻ was chosen as the anion, a novel catalyst [Mo₂V₂O₉(bpy)₆][PMo₁₁VO₄₀] was synthesized by hydrothermal method. This multi-isolated vanadium catalyst with a divanadium cation and a vanadium-substituted

* Corresponding author at: Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences, Dalian 116023, PR China. Tel.: +86 0411 84379248; fax: +86 0411 84379248.

** Corresponding author. Fax: +86 411 82159378.

E-mail addresses: sgao@dicp.ac.cn (S. Gao), wsyou@lnnu.edu.cn (W. You).

POM anion exhibited excellent catalytic performance for the hydroxylation of benzene to phenol.

2. Experimental

2.1. Materials

Disodium hydrogen phosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 99% purity) from Tianjin Kermel Chemical Reagent Co., Ltd., sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, 99% purity) from Tianjin Kermel Chemical Reagent Co., Ltd., sodium metavanadate ($\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$, 98% purity) from Tianjin Kermel Chemical Reagent Co., Ltd., tetramethylammonium hydroxide ($(\text{CH}_3)_4\text{NOH}$, 97% purity) from Aladdin Chemistry Co., Ltd., molybdenum trioxide (MoO_3 , 99.5% purity) from Shanghai Colloid Chemical Plant, vanadium pentoxide (V_2O_5 , 99% purity) from Tianjin Guangfu Fine Chemical Research Institute, 2,2'-bipyridine (bpy, $\text{C}_{10}\text{H}_8\text{N}_2$, 99% purity) from Sigma–Aldrich (Shanghai) Trading Co., Ltd., silicotungstic acid ($\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$, A. R.) from Tianjin Damao Chemical Reagent Factory were all used as received without further purification to produce catalysts. Benzene (C_6H_6 , 99.5% purity) from Beijing Chemical Works was used as substrate. Acetic acid (CH_3COOH , 99.5% purity) from Guangdong Guanghua Chemical Factory Co., Ltd., acetonitrile (CH_3CN , 99.5% purity) from Beijing Chemical Works, methanol (CH_3OH , 99.8% purity) from Sinopharm Chemical Reagent Beijing Co., Ltd., ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, 99.8% purity) from Sinopharm Chemical Reagent Beijing Co., Ltd., sulfolane ($\text{C}_4\text{H}_8\text{O}_2\text{S}$, G. R.) from Aladdin Chemistry Co., Ltd., dimethyl sulfoxide ($(\text{CH}_3)_2\text{SO}$, A. R.) from Aladdin Chemistry Co., Ltd. were used as solvents. Hydrogen peroxide (H_2O_2 , 35% purity) from Shanghai Yuanda Peroxide Co., Ltd. was used as the oxidant.

2.2. Catalyst preparation

2.2.1. Preparation of $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$

$\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$ was prepared according to reference [23]. 7.16 g (20 mmol) of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 3.16 g (20 mmol) of $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$ were added in 80 mL of water at 25 °C. 2 mL of 98% H_2SO_4 was added to the mixture above, 53.2 g (220 mmol) of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in 80 mL of water then mixed the two solutions. Another 34 mL of 98% H_2SO_4 was added into the solution. 160 mL of ethyl

ether was added to the mixture. $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$ was separated from the middle layer of the mixture then was characterized by IR spectra (Fig. S1a).

2.2.2. Preparation of $[\text{Mo}_2\text{V}_2\text{O}_9(\text{bpy})_6][\text{PMo}_{11}\text{VO}_{40}]$ (**1**)

1 was prepared by the hydrothermal method. 0.21 g of $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}] \cdot 19\text{H}_2\text{O}$, 0.073 g of MoO_3 , 0.018 g of V_2O_5 , 0.062 g of 2,2'-bpy and 10 mL distilled water were mixed and stirred, then the pH of the solution was adjusted to 4.8 with 2 M NaOH. The suspension was transferred into a 30 mL Teflon-lined autoclave and kept at 160 °C for 48 h. After the temperature was cooled slowly to 25 °C, orange crystals were obtained. The yield was 31% (based on Keggin anion). The catalyst was dried in vacuum at 80 °C for 24 h to remove the water. Elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{48}\text{N}_{12}\text{O}_{49}\text{PMo}_{13}\text{V}_3$ (3152.09): C 22.86, H 1.53, N 5.33. Found (%): C 22.80, H 1.57, N 5.30.

2.2.3. Preparation of $[\text{Mo}_2\text{V}_2\text{O}_9(\text{bpy})_6][\text{SiW}_{12}\text{O}_{40}]$ (**2**)

2 was prepared as **1** but added 0.28 g (0.1 mmol) of $\text{H}_4[\text{SiW}_{12}\text{O}_{40}] \cdot x\text{H}_2\text{O}$ instead of 0.21 g (0.1 mmol) of $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}] \cdot 19\text{H}_2\text{O}$ [22]. Based on W, 43% yield of crystals was obtained. The catalyst was dried in vacuum at 80 °C

for 24 h to remove the water. Elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{48}\text{N}_{12}\text{O}_{49}\text{SiMo}_2\text{V}_2\text{W}_{12}$ (4249.15): C 16.95, H 1.13, N 3.95. Found (%): C 16.94, H 1.17, N 3.93.

2.2.4. Preparation of $[(\text{CH}_3)_4\text{N}]_4[\text{PMo}_{11}\text{VO}_{40}]$ (**3**)

3 was prepared [24,25] by adding four equivalents of $(\text{CH}_3)_4\text{NOH}$ into the $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$ solution and was identified by IR spectra (Fig. S1b).

2.2.5. Synthesis of $[(\text{CH}_3)_4\text{N}]_4[\text{SiW}_{12}\text{O}_{40}]$ (**4**)

4 was prepared by adding four equivalents of $(\text{CH}_3)_4\text{NOH}$ to the $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ solution and was identified by IR spectra (Fig. S1c).

2.3. Catalyst characterization

The IR spectra of the catalysts were performed in the range 4000–400 cm^{-1} at the resolution of 4 cm^{-1} on a FT-IR Bruker NEXUS470 spectrometer with pressed KBr disks. The TG/DTA data of the catalysts were recorded on a Pyris Diamond TG/DTA instrument with a heating rate of 10 °C min^{-1} under immobile airflow. Crystal data of **1** were collected on a SMART APEX II-CCD X-ray single crystal diffractometer with graphite-monochromatic Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The elemental analyses of catalysts (C/H/N) were analyzed on a Perkin-Elmer 2400 CHN Elemental Analyzer.

2.4. Catalytic testing

The hydroxylation of benzene was carried out in a 25 mL flask equipped with a condenser. In a typical reaction, 0.0788 g (0.025 mmol) of **1**, 0.78 g (10 mmol) of benzene and 2.83 g (30 mmol) of 35% H_2O_2 were added into 6.8 mL of acetonitrile. The flask was put into a water bath at 80 °C for 2 h. After reaction, 0.2 g of toluene was added as the internal standard. The GC analysis of the samples were recorded on a GC-Agilent 7890 series instrument equipped with an Agilent SE-30 capillary column and a flame ionization detector.

$$\text{Yield of phenol}(\%) = \frac{\text{phenol}}{\text{initial benzene}} \times 100\%.$$

$$\text{Selectivity to phenol}(\%) = \frac{\text{phenol}}{\text{phenol} + \text{benzoquinone} + \text{catechol} + \text{hydroquinone} + \text{maleic anhydride}} \times 100\%.$$

3. Results and discussion

3.1. Catalyst characterization

3.1.1. FT-IR spectral studies

When a mixture of MoO_3 , V_2O_5 , bpy and $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ has been heated to 180 °C for 2 days under the hydrothermal condition, orange crystals can be achieved. These crystals were washed by water for several times, then were dried and characterized by FT-IR. The FT-IR spectra of **1** (Fig. 1) with the peaks at 951 cm^{-1} , 868 cm^{-1} and 798 cm^{-1} were attributed to the $\nu_{\text{as}}(\text{Mo}-\text{O}_t)$, $\nu_{\text{as}}(\text{Mo}-\text{O}_b-\text{Mo})$ and $\nu_{\text{as}}(\text{Mo}-\text{O}_c-\text{Mo})$ for the Keggin structure, while the peaks at 1071 cm^{-1} and 1055 cm^{-1} were attributed to the $\nu(\text{P}-\text{O})$ [26]. Peaks at 1606 cm^{-1} and 759 cm^{-1} were caused by the $\nu(\text{C}-\text{C})$ and $\phi(\text{C}-\text{C})$ of bpy ligand, while the ring breathing of bpy ligand caused the peak at 994 cm^{-1} [27].

3.1.2. Thermal analysis

The TG/DTA analysis was carried out to investigate the thermal stability of **1**. As shown in Fig. 2, the crystal water of **1** led to the weight loss (2.50%) below 400 °C. The weight loss in the range of

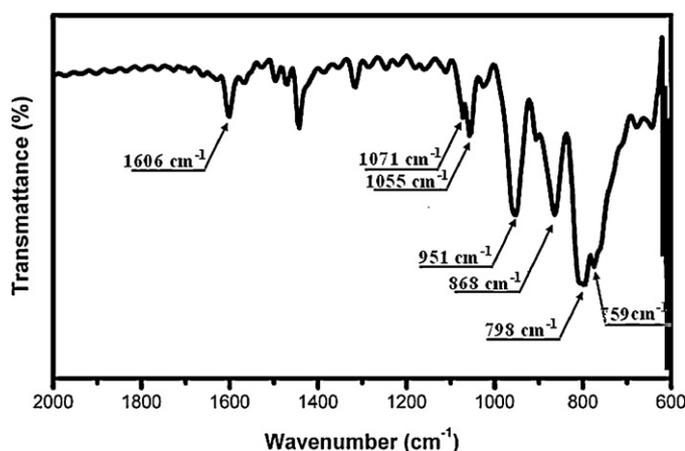


Fig. 1. FT-IR spectra of **1**.

400–520 °C was 28.75%, which may be caused by the decay of bpy ligand (calc. was 29.69%).

3.1.3. X-ray single crystal diffraction studies

X-ray single crystal diffraction elucidated the precise structure of **1**, which consisted of Mo/V/O-based cation $[\text{Mo}_2\text{V}_2\text{O}_9(\text{bpy})_6]^{4+}$ and Keggin heteropolyanion $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$ (Fig. 3). The complex cation $[\text{Mo}_2\text{V}_2\text{O}_9(\text{bpy})_6]^{4+}$ exhibited an tetranuclear Z-shaped organic–inorganic hybrid structure (Fig. S2). Via V–O–Mo–O–Mo–O–V mode, the Z-shaped chains consisted of corner-sharing $\{\text{MoO}_4\text{N}_2\}$ and $\{\text{VO}_2\text{N}_4\}$ octahedra. Bpy ligands were coordinated directly to Mo and V centers. According to the bond valence sum calculations as well as charge balance [28], in $[\text{Mo}_2\text{V}_2\text{O}_9(\text{bpy})_6]^{4+}$ and the Keggin anion $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$ of **1**, V atoms were in their +5 oxidation state.

3.2. Catalytic activity tests

3.2.1. Effect of solvents

Solvent has a powerful influence on the liquid hydroxylation of benzene to phenol (Table 1). Acetonitrile (Table 1, Entry 1) and acetic acid (Table 1, Entry 2) matched the catalyst well, with the phenol yields of 10.0% and 9.4%, respectively. Only in acetic acid, **1** played the role as a homogeneous catalyst, which might be due to a chemical change of the catalyst. In the other solvents, **1** played the role as a heterogeneous catalyst. Sulfolane can often be used as the solvent for hydroxylation of benzene to phenol

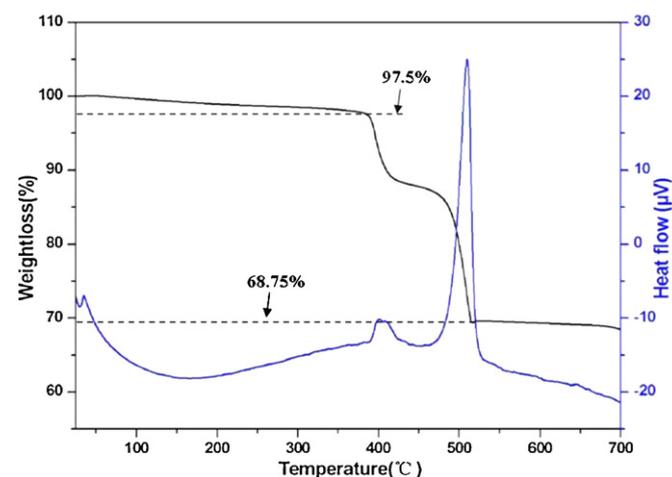


Fig. 2. TG/DTA curves of **1**.

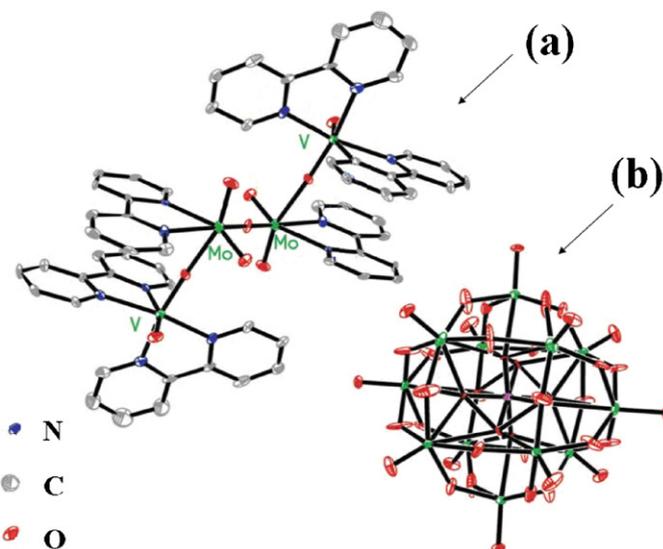


Fig. 3. Molecular structure of **1**, (a) $[\text{Mo}_2\text{V}_2\text{O}_9(\text{bpy})_6]^{4+}$, (b) $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$. Thermal ellipsoids set at 50% probability.

Table 1

Catalytic performance of **1** with different solvents.^a

Entry	Solvents	Phenol yield (%)	Product selectivity (%) ^c			
			MA	BQ	PH	CA
1	Acetonitrile	10.0	0	0	>99	0
2	Acetic acid	9.4	0	0.9	>99	0
3	Sulfolane	4.1	0	2.6	45.2	45.4
4	Ethanol	1.8	0	0	>99	0
5	Water	1.2	0	36.0	64.0	0
6 ^b	None	1.1	1.4	72.4	26.2	0

^a Reaction conditions: benzene/**1** molar ratio = 400/1, 0.78 g (10 mmol) of benzene, 1.42 g (15 mmol) of 35% H_2O_2 , solvent 6.8 mL, temperature = 60 °C, 240 min.

^b 2.83 g (30 mmol) of 35% H_2O_2 .

^c MA = maleic anhydride, BQ = benzoquinone, PH = phenol, CA = catechol, HY = hydroquinone.

catalyzed by TS-1. However, the phenol yield was only 4.1% (Table 1, Entry 3) when using sulfolane as the solvent, the by-products benzoquinone, catechol and hydroquinone were all detected. The solvent-free condition (Table 1, Entry 6) was also investigated but the phenol yield was only 1.1% with a low selectivity to phenol of 26.2%.

3.2.2. Effect of reaction time and temperature

When the amount of H_2O_2 increased from 15 mmol to 30 mmol, higher phenol was obtained (Fig. 4, 60 °C, 240 min). Thus, the amount of H_2O_2 was one of the principal factors for the synthesis of phenol. The catalytic activities of **1** were obviously enhanced under higher temperatures. The yield of phenol reached 25.5% at 80 °C in the initial 120 min, while it decreased with time prolonged (Fig. 4). At 60 °C, even the reaction time prolonged to 240 min, the yields of phenol remained below 20%. At the lower temperature of 40 °C, the phenol yields were still negligible during the 240 min.

3.2.3. Effect of H_2O_2 amount

In the hydroxylation of benzene to phenol, an excess of H_2O_2 is used and the H_2O_2 decomposition is taken into account. The rate of hydroxylation catalyzed by **1** is highly sensitive to H_2O_2 amount. Increasing H_2O_2 amount from the initial value of 10 mmol to 30 mmol increased the phenol yield from 2.8% (Table 2, Entry 1) to 25.4% (Table 2, Entry 3), accordingly, the H_2O_2 efficiency increased from 2.8% to 8.5%. Further increasing the H_2O_2 amount led to a slight decrease in phenol yield (Table 2, Entry 4).

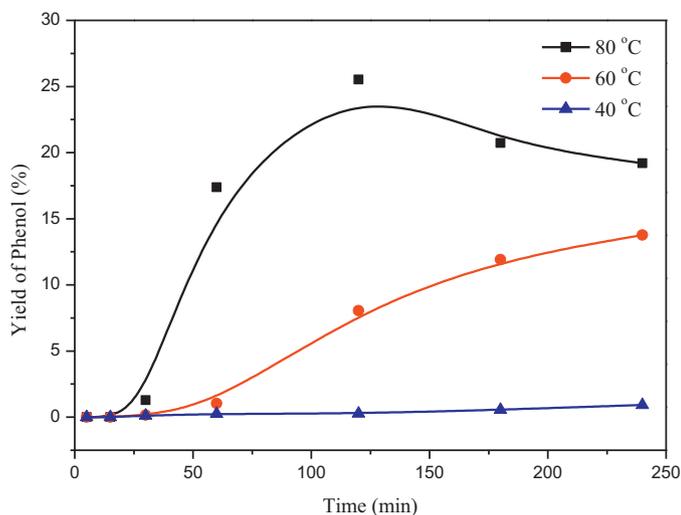


Fig. 4. The effect of reaction time under different temperatures. Reaction conditions: benzene/1 molar ratio = 400/1, 0.78 g (10 mmol) of benzene, acetonitrile 6.8 mL, 2.83 g (30 mmol) of 35% H₂O₂, temperatures were 40 °C, 60 °C and 80 °C.

Table 2
H₂O₂ efficiency catalyzed by **1** with different H₂O₂ amount.^a

Entry	H ₂ O ₂ amount (mmol)	H ₂ O ₂ conversion (%)	H ₂ O ₂ efficiency (%) ^b	Phenol yield (%)
1	10	>99.9	2.8	2.8
2	20	>99.9	4.2	8.4
3	30	>99.9	8.5	25.4
4	40	>99.9	5.7	22.6

^a Reaction conditions: benzene/1 molar ratio = 400/1, 0.78 g (10 mmol) of benzene, acetonitrile 6.8 mL, temperature = 80 °C, 120 min.

^b Moles of phenol/moles of reacted H₂O₂ × 100%.

3.2.4. Effect of different catalysts

In order to further investigate the catalytic performance of **1**, control experiments were performed with the same vanadium content (benzene/total vanadium = 400/3). The yield of phenol catalyzed by **2** reached up to 16.3% (Table 3, Entry 1), which showed that the cationic [Mo₂V₂O₉(bpy)₆]⁴⁺ definitely had catalytic activities. The phenol yield catalyzed by **3** reached up to 16.8% (Table 3, Entry 2). From the control experiment catalyzed by **4** (Table 3, Entry 3), it yielded nothing showed that neither cationic

Table 3
The effect of different catalysts.^a

Entry	Catalysts (mol ratio of benzene/catalysts)	Phenol yield (%)	Product selectivity (%) ^b				
			MA	BQ	PH	CA	HY
1	Benzene/2 = 800/3	16.3	5.1	0	88.2	0.8	5.9
2	Benzene/3 = 400/3	16.8	7.4	0	84.0	0	8.6
3 ^c	Benzene/4 = 400/1	0	–	–	–	–	–
4	Benzene/2/3 = 400/1/1	17.6	3.5	0.2	87.1	0.4	8.8
5	Benzene/1 = 400/1	25.5	3.8	0	90.7	0.7	4.8

^a Reaction conditions: 0.78 g (10 mmol) of benzene, acetonitrile 6.8 mL, 2.83 g (30 mmol) of 35% H₂O₂, 80 °C, 120 min.

^b MA = maleic anhydride, BQ = benzoquinone, PH = phenol, CA = catechol, HY = hydroquinone.

^c 1.42 g (15 mmol) of 35% H₂O₂, 60 °C, 240 min.

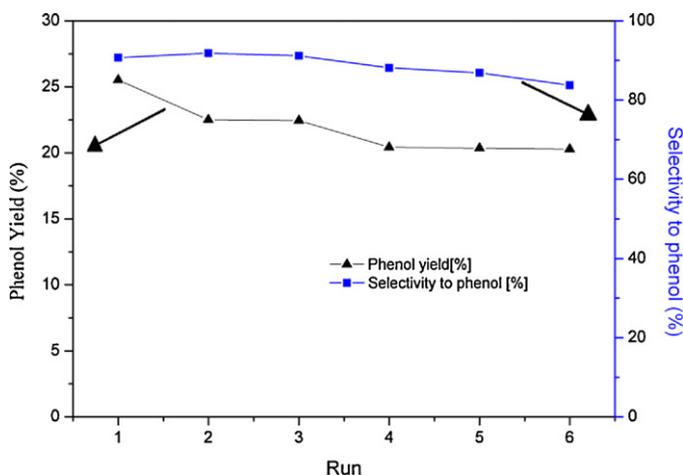


Fig. 5. Recycle performance of **1**. Reaction conditions: benzene/1 molar ratio = 400/1, benzene 10 mmol, acetonitrile 6.8 mL, 35% H₂O₂ 30 mmol, 80 °C, 120 min. Reaction mixture was centrifuged after each reaction, the reaction solution was removed, reactants (except the catalyst) were recharged to carry out the next run.

[(CH₃)₄N]⁺ nor anionic [SiW₁₂O₄₀]⁴⁻ has hydroxylation activities. When **2** and **3** were used together, the yield of phenol was just a little increased to 17.6% (Table 3, Entry 4). It seemed that the hydroxylation performance can not be obviously enhanced by the mechanical mixing of the two active catalysts. The active

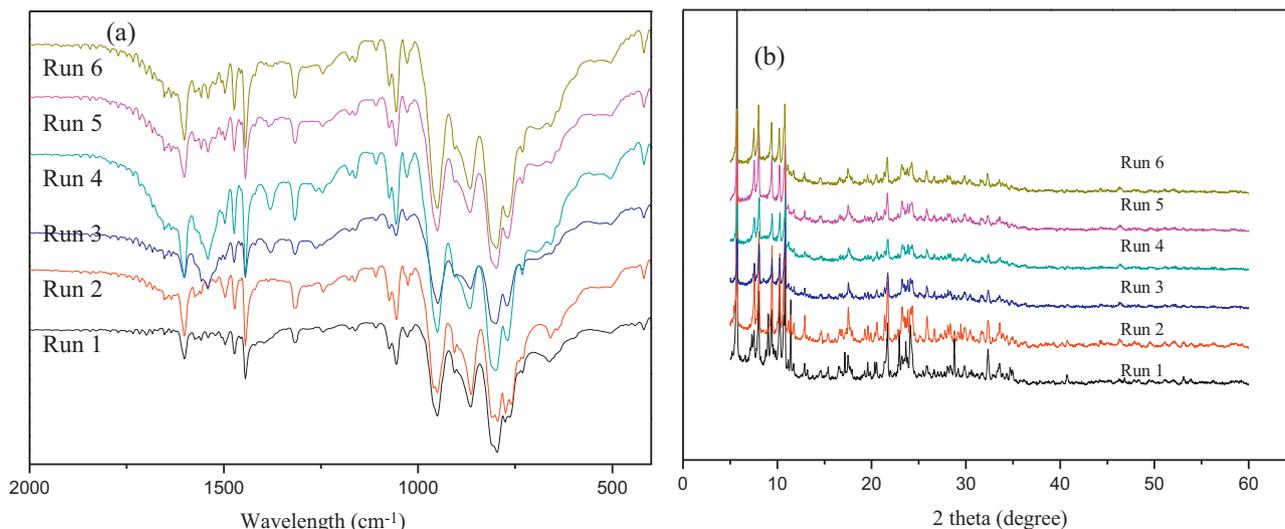


Fig. 6. (a) IR of recycled **1** and (b) XRD of recycled **1**.

cationic $[\text{Mo}_2\text{V}_2\text{O}_9(\text{bpy})_6]^{4+}$ of **2** and the anionic $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$ of **3** were together assembled into **1** showed satisfactory performance for the hydroxylation of benzene to phenol (Table 3, Entry 5), which was likely to be caused by the combination of cationic $[\text{Mo}_2\text{V}_2\text{O}_9(\text{bpy})_6]^{4+}$ and anionic $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$, and the increased amount of multi-isolated active sites.

3.3. Catalytic stability and recyclability

As a heterogeneous catalyst, **1** was insoluble in acetonitrile and its recycle abilities were evaluated. The activities of the catalysts decreased in the first run, in the next five recycles, the decrease of the catalysts performance was unobvious (Fig. 5). The selectivities to phenol slightly drop in the next five recycles, it may be caused by the further oxidation of the products and the coking on the catalysts surface.

In order to check the stability of **1**, IR and XRD were also performed after each run. In the first reaction and further 5 recycles, as shown in Fig. 6(a), the characteristic peaks in IR spectra for Keggin structure and bpy ligands were unchanged, which showed that the molecular structure of **1** was remained. As shown in Fig. 6(b), the position of each peak in XRD patterns was unchanged, which showed that the crystal structure of **1** was unchanged.

4. Conclusions

In conclusion, a novel multi-vanadium-containing POMs catalyst, in which the active sites are located in both of its cationic and anionic parts, has been successfully synthesized by the hydrothermal method. This catalyst exhibited better performance than the traditional POMs catalysts, higher yield of phenol and higher selectivity to phenol were achieved. This catalyst also has good stability and high recoverability in the hydroxylation of benzene to phenol. We hope this effort we have made can provide a clue for the preparation of multi-isolated active sites POMs catalysts.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcata.2013.03.009>.

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