

# Direct hydroxylation of benzene to phenol by supported vanadium substitution polyoxometalates using $\text{H}_2\text{O}_2$ as oxidant

Yingwei Yang<sup>1</sup> · Ruiren Tang<sup>1</sup>

Received: 1 February 2018 / Accepted: 4 May 2018 / Published online: 26 May 2018  
© Springer Science+Business Media B.V., part of Springer Nature 2018

**Abstract** A practical method for the direct hydroxylation of benzene to phenol catalyzed by supported vanadium-substituted polyoxometalates using  $\text{H}_2\text{O}_2$  as an oxidant is described. Three vanadium-doped polyoxometalate  $\text{Na}_2\text{H}_3\text{PMo}_{10}\text{V}_2\text{O}_{40-x}\text{H}_2\text{O}$  catalysts were designed and prepared through support on graphitic carbon nitride (g- $\text{C}_3\text{N}_4$ ), montmorillonite, and activated carbon and named as CN-PMoV<sub>2</sub>, M-PMoV<sub>2</sub>, and C-PMoV<sub>2</sub>, respectively. Their characterization was elucidated through the Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), inductively coupled plasma-atomic emission spectrometry (ICP-AES) and scanning electron microscopy (SEM). This heterogeneous catalyst demonstrated promising activity in the hydroxylation of benzene to phenol with  $\text{H}_2\text{O}_2$ . Especially, CN-PMoV<sub>2</sub> catalyst was highly active and selective even under mild conditions. Moreover, CN-PMoV<sub>2</sub> catalyst still has a certain catalytic effect even after three instances of repeated use.

**Keywords** Vanadium-doped polyoxometalates · Supported · Oxidation · Hydroxylation of benzene

## Introduction

Phenol, as one of the most important chemicals, has been widely used in phenol resins, related pharmaceuticals, dyes, antioxidants, and bisphenols [1–4]. Traditional industrial production (above 90%) of phenol utilizes a three-step process with high energy consumption and low yield, inevitably resulting in some environmental

---

✉ Ruiren Tang  
trr@mail.csu.edu.cn

<sup>1</sup> School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, Hunan, China

problems [5]. Direct hydroxylation of benzene to phenol is recognized as the most practical method in chemical industry. However, the  $\text{Csp}^2\text{-H}$  bonds are kinetically inert and thermodynamically strong [6], and, at the same time, the hydroxy group of phenol is easily over-oxidized in the reaction. Therefore, the production of phenol via direct activation of a  $\text{C-H}$  bond from benzene has been a topic of potential interest [7–11] and a challenging assignment [12–14].

In the last two decades, remarkable achievement has been witnessed in one-step hydroxylation of benzene to phenol with  $\text{O}_2$  [15–21] and  $\text{N}_2\text{O}$  in gaseous phase [22–24]. Meanwhile, many scientists have focused on direct hydroxylation of benzene to phenol in liquid phase with  $\text{H}_2\text{O}_2$  as the environmentally benign oxidant; this process is inexpensive, readily available, can be handled concisely, and only produces water as by-product [25–28].

Heteropoly acids with a tunable structure at the molecular level are used in catalytic reaction and in designing compounds exhibiting special characteristics such as facilely modified acid–base properties and redox potential. There have some achievements in hydroxylation of benzene to phenol [29]. Vanadium is an efficient catalytic element; the catalytically active center of V-containing Keggin-type heteropoly acids contain vanadium(IV) or vanadium(V) and are capable of mutual transformation through electron transfer. During this process, the  $\text{Csp}^2\text{-H}$  bond is activated and the direct result is that benzene can be oxidized by oxidants [30]. For the same reaction, catalyst state, and post-treatment of the heterogeneous catalysis, the catalytic reaction usually takes place on a solid surface, and the substrate needs to be sufficiently diffused to the active site and react adequately at the boundary layer. The products also need to be desorbed from the surface by the reverse process, which relates to the pore structure, such as pore size, volume, distribution, and the micro-environmental state of the surface. These features can affect the catalytic activity and selectivity significantly and are generally different from the homogeneous reaction. Immobilization of heteropolyacids with catalytically active compounds is an effective and easy heterogeneous catalytic strategy.

Recently, a dual-catalysis non-noble metal system has received great attention [31]; the system uses graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ) and Keggin-type polyoxometallate  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$  as catalyst and  $\text{LiOAc}$  as an effective additive. In this catalytic system, effective catalytic components are composed of several substances including  $\text{g-C}_3\text{N}_4$ ,  $\text{PMoV}_2$ , and  $\text{LiOAc}$ . However, the yield of hydroxylation of benzene to phenol is 13.6% using that catalyst. In this work, we have prepared a reductant-free supported polyoxometallate heterogeneous catalyst system to oxidize benzene to phenol, leading to a higher conversion rate and selectivity than those of the reported catalysts. Heteropoly acid compounds were synthesized according to reported literatures [32] and we selected three kinds of carriers including carbon nitride ( $\text{g-C}_3\text{N}_4$ ), montmorillonite, and activated carbon to support the heteropoly acid salt as catalyst. Direct hydroxylation of benzene to phenol is then reported.

Meanwhile, some of the reaction conditions were optimized. We focused on the catalytic performance of  $\text{CN-PMoV}_2$  because  $\text{g-C}_3\text{N}_4$  has a strong binding charge capacity conducive to the stable transition of charged intermediates to the product as compared to the other two carriers.

## Experimental

### Chemicals

All solvents and reagents of analytical reagent (AR) grade were purchased commercially from Aladdin and used without further purification. Phosphomolybdic acid, sodium metavanadate, molybdenum trioxide, phosphoric acid (85%, by mass, aqueous solution), melamine, montmorillonite, activated carbon, benzene, acetonitrile, acetic acid, hydrogen peroxide (30%, by mass, aqueous solution), and tap water were deionized before use.

### Preparation of the $\text{Na}_2\text{H}_3\text{PMo}_{10}\text{V}_2\text{O}_{40} \cdot x\text{H}_2\text{O}$

Vanadium-substituted molybdophosphorus heteropoly acid sodium salt  $\text{Na}_2\text{H}_3\text{PMo}_{10}\text{V}_2\text{O}_{40} \cdot x\text{H}_2\text{O}$  ( $\text{PMoV}_2$ ) was prepared according to the reported methods [33]. Briefly, 14.40 g (0.10 mol) of  $\text{MoO}_3$  and 2.44 g of  $\text{NaVO}_3$  (0.02 mol) were added into a 500-mL three-necked flask. Then, 250 mL of deionized water was added and the resulting suspension was stirred at reflux. Then, 1.15 g (85%, by mass) of phosphoric acid dissolved in 10.00 mL of water was added dropwise to the previous suspension. After 24 h of vigorous stirring, an orange-red clear solution was obtained. Finally, water was distilled off at 100 °C under reduced pressure and an orange-red solid powder was obtained. The  $\text{PMoV}_2$  was purified by recrystallization with water.

### Preparation of the $\text{C}_3\text{N}_4$

According to the literature [34], the mesoporous carbon nitride ( $\text{C}_3\text{N}_4$ ) carrier was prepared by thermal polymerization of melamine. Typically, 5.00 g of melamine was added to a crucible with a cover, the temperature was raised to 550 °C at a heating rate of 3 °C/s in a muffle furnace and maintained for 4 h. After sufficient reaction and cooling to room temperature,  $\text{C}_3\text{N}_4$  powder was obtained by grinding the light-yellow block solid.

### Preparation of the Supported Catalyst

Preparation of CN- $\text{PMoV}_2$  involves dissolving 1 g of  $\text{PMoV}_2$  in 25 mL of deionized water, adding 5 g of  $\text{C}_3\text{N}_4$ , ultrasound for 15 min, then, reflux for 24 h in an oil bath. After full load, filtration, and washing, the light-yellow-green product was obtained. The powder was calcined in a crucible at 550 °C for 2 h, giving CN- $\text{PMoV}_2$ . The M- $\text{PMoV}_2$  was prepared using the same method ( $\text{PMoV}_2$  load on montmorillonite). It was not required to roast for the preparation of C- $\text{PMoV}_2$  which is different from that of the former.

## Characterization methods

FT-IR spectra were determined on a Nicolet NEXUS 670 FT-IR spectrophotometer using KBr discs in the 400–4000-cm<sup>-1</sup> region under atmospheric conditions. Inductively coupled plasma (ICP) was measured with an Optima 5300 DV ICP-optical emission spectrometry system and the heterogeneous samples were preprocessed by acid digestion with hydrochloric acid. The reaction products of oxidation were monitored using a GC-7890II gas chromatograph (GC) with an OV-1701 column (50 m × 0.25 mm × 0.25 μm) in a flame ionization detector (FID). Thermogravimetric analysis (TGA) measurements were determined with a NETZSCH STA 449 thermal analyzer using an α-Al<sub>2</sub>O<sub>3</sub> crucible. Scanning electron microscopy (SEM) images were recorded with an FEI QUANTA 200 microscope. The pore diameter and specific surface area of the materials were measured with a Beishide 3H-2000BET-A tester at 77 K.

## Catalytic test

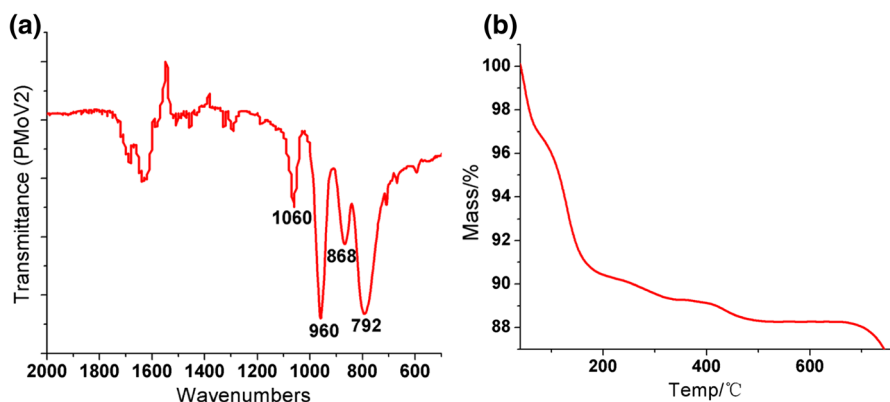
The hydroxylation of benzene to phenol is as follows: catalyst (CN-PMoV<sub>2</sub> 0.10 g) was added to a 25-mL round-bottom flask, with 5.00 mL of acetic acid and 5.00 mL of acetonitrile as solvent, 1 mL of benzene (12.2 mmol), and 3.4 mL of H<sub>2</sub>O<sub>2</sub> (30%, 34 mmol) added successively. After mixing the reaction substrate at room temperature, the reaction was conducted at 80 °C for 20 h with vigorous stirring in an oil bath. After completion of the reaction, the mixture was filtered to remove the solid catalyst for the next reaction after cleaning and drying. Simultaneously, the liquid mixture was analyzed by GC with an FID and a capillary column (SE-54; 50 m × 0.25 mm × 0.25 μm). The temperature of the GC column oven was kept at 60 °C for 2 min and then increased to 180 °C at a rate of 8 °C/min; injection temperature and detection temperature were set at 240 and 180 °C, respectively.

## Results and discussion

### Characterization of the catalyst

Heteropoly acid with Keggin structure appears on four obvious characteristics peaks in the range of 1100–700 cm<sup>-1</sup>. The FT-IR spectra of Na<sub>2</sub>H<sub>3</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> is presented in Fig. 1a. The four characteristic bands for the Keggin structure of Na<sub>2</sub>H<sub>3</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> appear at 1060 (P–O<sub>a</sub>), 960 (Mo–O<sub>d</sub>), 868 (Mo–O<sub>b</sub>–Mo), and 792 (Mo–O<sub>c</sub>–Mo) cm<sup>-1</sup>, respectively [35].

TGA of Na<sub>2</sub>H<sub>3</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> was performed in nitrogen atmosphere at a scanning of 12 °C/min between 40 and 800 °C and shown in Fig. 1b. The resulting heteropoly acid has four weight-loss processes, corresponding to loss of adsorbed water, crystal water, combined with water, and structured water, respectively. A small amount of quality reduction of PMoV<sub>2</sub> before 100 °C resulted from the loss of the adsorbed water [36]; 100–200 °C loss of the crystal water; 200–350 °C and 350–500 °C loss of the combined with water and structured water, respectively.



**Fig. 1** The FT-IR spectra and thermogravimetric analysis of  $\text{Na}_2\text{H}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}$

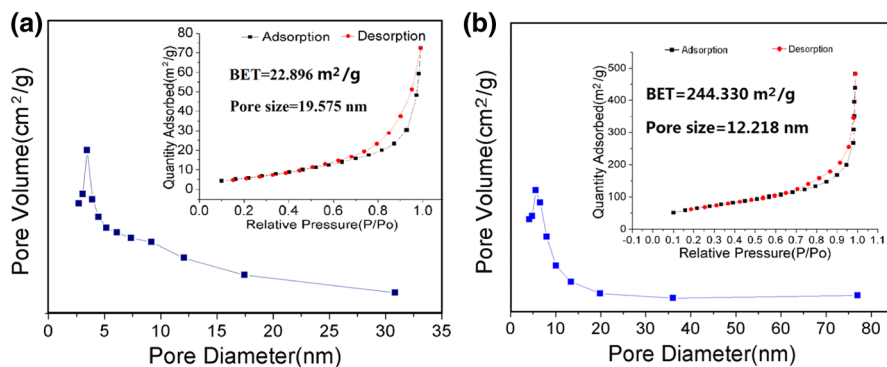
The metal element content of the catalyst was quantitatively analyzed by ICP-atomic emission spectroscopy (ICP-AES). The results are shown in Table 1. It was found that the molar ratio of Mo-to-P was 9.91 and the molar ratio of V-to-P was 2.01, which was close to stoichiometric ratios of 10 and 2; that is to say, the synthetic sodium phosphomolybdate has a higher purity.

To obtain textural properties of the  $g\text{-C}_3\text{N}_4$  support (Fig. 2a inset) and the as-prepared  $\text{CN-PMoV}_2$  (Fig. 2b inset) catalyst, the isotherms and the Barrett–Joyner–Halenda (BJH) pore size distributions were recorded. The nitrogen adsorption–desorption isotherm curves reveal a surface area of  $22.896\text{ m}^2/\text{g}$  and type IV adsorption isotherms, revealing the mesoporous structure of the  $g\text{-C}_3\text{N}_4$ . The BJH desorption average pore diameter is  $19.575\text{ nm}$ . After the loading of  $\text{PMoV}_2$ , the isotherm shape and the pore diameter of the  $\text{CN-PMoV}_2$  were slightly smaller compared with that of the  $g\text{-C}_3\text{N}_4$ , indicating that the  $\text{PMoV}_2$  did not block the pore distribution and Brunauer–Emmett–Teller (BET) surface area made a big increase, up to  $244.330\text{ m}^2/\text{g}$ , indicating adsorption on the surface successfully and increasing the BET surface area after introduction of  $\text{PMoV}_2$ .

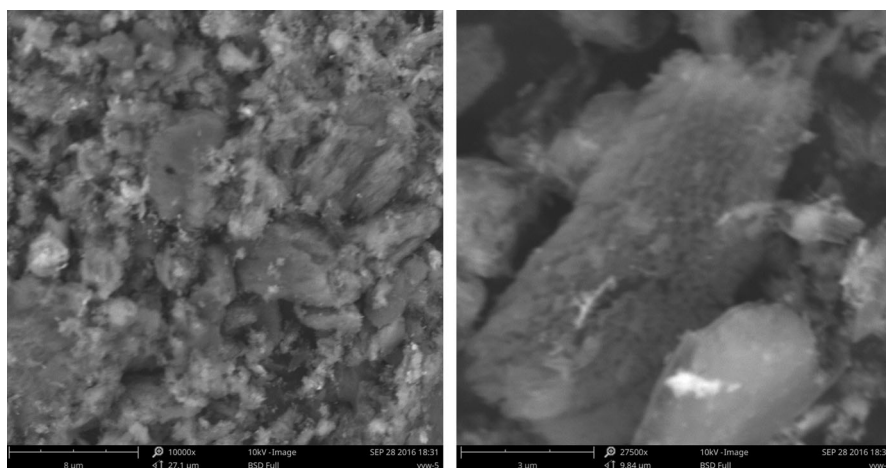
In the microstructure of  $g\text{-C}_3\text{N}_4$  and  $\text{CN-PMoV}_2$ , based on SEM analysis (Fig. 3), the carrier adsorbs the heteropolyacid salt catalyst as the active site on the surface evenly, in which outward expansion makes the specific surface area much larger than the carrier.

**Table 1** Elemental analysis of the catalyst

Catalyst	Mass fraction (%)				Molar ratio	
	P	Mo	V	Na	Mo-to-P	V-to-P
$\text{Na}_2\text{PMoV}_2$	1.74	53.9	5.74	2.59	9.91	2.01



**Fig. 2** Pore size and particle size distribution characterizations of the catalyst



**Fig. 3** Scanning electron microscopy of  $g\text{-C}_3\text{N}_4$  and CN-PMoV<sub>2</sub>

### Catalytic performance of direct hydroxylation of benzene to phenol

Heterogeneous catalysis for the aerobic oxidation of benzene to phenol by the supported polyoxometallate catalyst without a reducing agent was investigated. At first, the carried material vanadium-substituted phosphomolybdic heteropolyacids on the catalytic reaction were studied with results shown in Table 2. No phenol was obtained when we conducted the reaction without catalyst (entry 1) or with the V-free phosphomolybdic acid (entry 2).

As shown in Table 2, no phenol was obtained when no vanadium-substituted heteropoly acid compound was used (entry 2). The hydroxylation of benzene to phenol with hydrogen peroxide by PMoV<sub>2</sub> in a homogeneous reaction produced less than 5.0% phenol with conversion of benzene at 10.1% (entry 3). This demonstrated that V is indispensable to catalyze benzene hydroxylation to phenol with H<sub>2</sub>O<sub>2</sub>. Similar yields (29.0–30.5%) of phenol were obtained using C-PMoV<sub>2</sub> (entry 5) and

**Table 2** Performance of catalysts for the hydroxylation of benzene to phenol with H<sub>2</sub>O<sub>2</sub>

Entry	Catalysts	Conversion of benzene (%)	Yield to phenol (%)	Selectivity for phenol (%)
1	None	0	0	–
2	H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	0	0	–
3	PMoV <sub>2</sub>	10.1	< 5.0	–
4	CN-PMoV <sub>2</sub>	38.9	38.8	> 99.0
5	M-PMoV <sub>2</sub>	37.5	30.5	81.2
6	C-PMoV <sub>2</sub>	32.6	29.9	91.8

*Reaction conditions* catalyst (100 mg), benzene (1 mL, 11.22 mmol), acetonitrile (5.00 mL), acetic acid (5.00 mL), H<sub>2</sub>O<sub>2</sub> (30 wt%, 3.40 mL, 33.90 mmol), 80 °C, 20 h; the results of the reaction were measured by GC

M-PMoV<sub>2</sub> in heterogeneous reactions (entry 6). In addition, it can be seen that CN-PMoV<sub>2</sub> provided a satisfactory conversion rate of 38.9% and the selectivity was over 99.0% using H<sub>2</sub>O<sub>2</sub> as the oxidant (entry 4) compared to its latter two (entries 5, 6). The results showed that the role of vanadium is indispensable in the catalytic process, in which the catalytic performance is far superior to vanadium-free heteropoly compounds. Then, the loading process greatly improves the catalytic activity and the selectivity of phenol.

Oxygen, *t*-butylhydroperoxide (TBHP), and H<sub>2</sub>O<sub>2</sub> were chosen as oxidants in our study (entries 1, 2, and 3, respectively). Among the three oxidants, hydrogen peroxide is the most efficient one compared to other two oxidants, oxygen, or TBHP (Table 3, entries 1, 2, and 3). Further optimization of different solvents, it was found the mixed solvent of acetic acid and acetonitrile is the most efficient compared to the individual acetic acid or acetonitrile (Table 3, entries 3, 4, 5), which maybe contributed to the fact strong acidity conditions can accelerate the decomposition of H<sub>2</sub>O<sub>2</sub> and thus reduce the yield of phenol, while weak acid environment can increase the yield. In addition, no phenol is detected in the solvent-free reaction [37] (entry 5).

**Table 3** Oxidizing agent and solvent for the hydroxylation of benzene to phenol

Entry	Oxide	CH <sub>3</sub> CN/ HA <sub>C</sub>	Conversion of benzene (%)	Yield to phenol (%)	Selectivity for phenol (%)
1	Oxygen	1:1	< 1.0	–	–
2	TBHP	1:1	< 1.0	–	–
3	H <sub>2</sub> O <sub>2</sub>	1:1	38.9	38.8	> 99.1
4	H <sub>2</sub> O <sub>2</sub>	1:0	8.5	7.1	84.0
5	H <sub>2</sub> O <sub>2</sub>	0:1	23.9	21.4	89.3
6	H <sub>2</sub> O <sub>2</sub>	–	< 5.0%	< 1.0	–

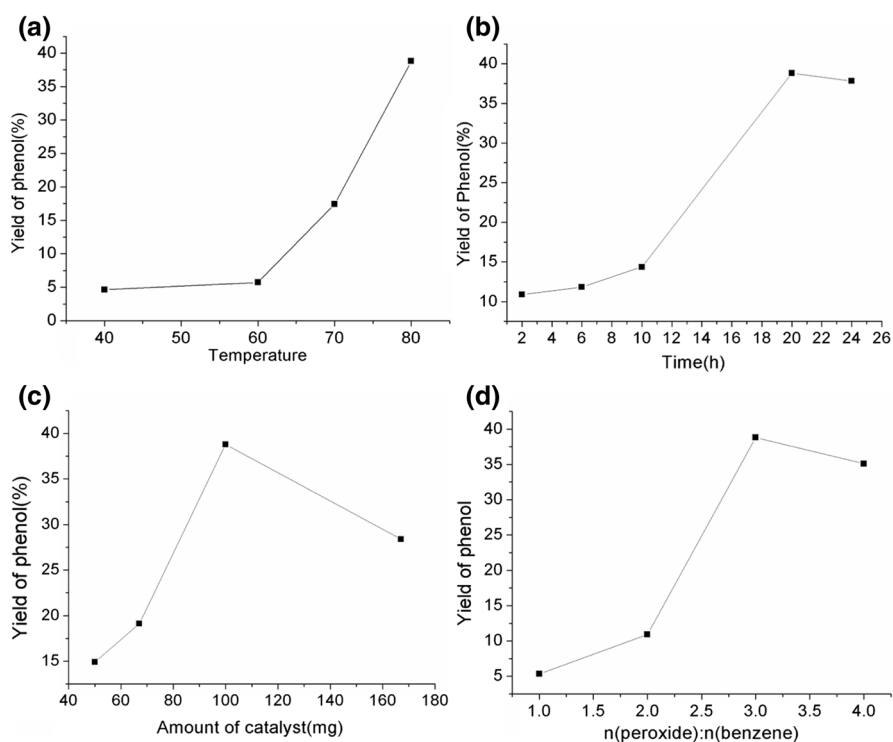
*Reaction conditions* catalyst (100 mg), benzene (1 mL, 11.22 mmol), 80 °C, 20 h

## Reaction temperature

The reaction temperature was studied and the results are shown in Fig. 4a. As we can see from Fig. 4a, the yield of phenol is extremely low when the temperature is below 60 °C, while the yield of phenol increases rapidly from 17.4 to 38.8% when the temperature increases from 60 to 80 °C. Therefore, we choose 80 °C as an optimum temperature for this catalytic system.

## Reaction time

The optimum reaction time was studied and the results are shown in Fig. 4b: The conversion of benzene to phenol was significantly low in the first 6 h with 15.1% of yield. In the second 6 h, the yield continues to increase, while after 20 h, the yield increased to 38.8% dramatically. Then, the yield starts to decrease, indicating that the phenol was oxidized after 20 h.



**Fig. 4** **a** Reaction temperature, **b** reaction time, **c** catalyst amount, and **d** hydrogen peroxide amount for hydroxylation of benzene to phenol with  $\text{H}_2\text{O}_2$



### Catalyst amount

We investigated the catalyst amount for the reaction and the results are shown in Fig. 4c. From Fig. 4c., we found the yields of phenol increased gradually from 14.9 to 38.8% when the amount of catalyst was increased from 50 to 100 mg. However, the yield of phenol showed a downward trend as the amount of catalyst continued to increase (more than 100 mg). Therefore, it was found 100 mg is the best amount of catalyst in our exploration, probably due to the fact  $\text{H}_2\text{O}_2$  can be quickly decomposed when adding more catalyst.

### Hydrogen peroxide amount

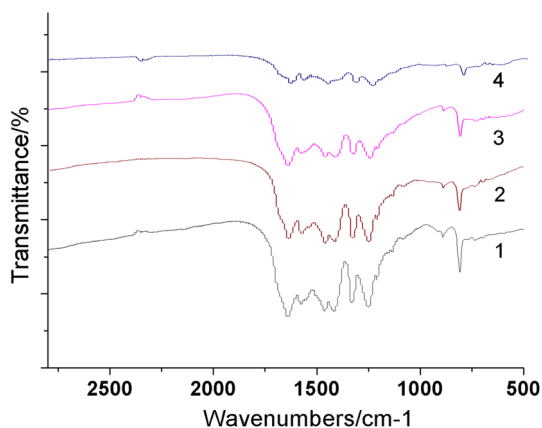
The effect of the amount of hydrogen peroxide on the yield of phenol is shown in Fig. 4d. As we can see from Fig. 4d, the yield of phenol increased rapidly from around 5.1 to 38.8% as the molar ratio of hydrogen peroxide to benzene was increased from 1 to 3 eq, while the yield was significantly decreased when the amount of hydrogen peroxide was increased from 3 to 4 eq. Possible reasons are as follows: the catalyst accelerates the decomposition of hydrogen peroxide when catalyzing the hydroxylation of benzene to phenol; the direct result is that only part of the hydrogen peroxide added to the reaction system is involved in the hydroxylation of benzene to phenol. In addition, too much hydrogen peroxide further oxidizes phenol to other byproducts and leads to a decrease in the overall yield of phenol. Our exploration indicates the yield of phenol is maximized when the molar ratio of hydrogen peroxide to benzene is three.

### Catalyst reusability

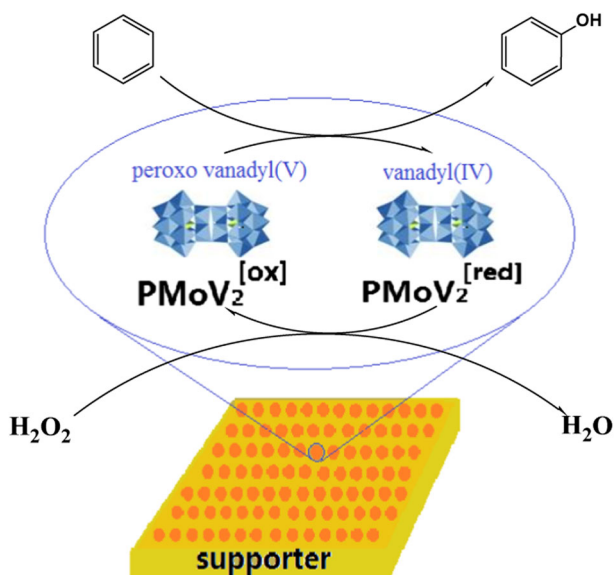
The reusability of CN-PMoV<sub>2</sub> catalyst was tested and the results showed that it can be easily recovered by direct filtration. Further, the catalytic capacity of recovered CN-PMoV<sub>2</sub> catalyst was studied. Expectedly, we found that this catalyst can be repeatedly used up to 3 times during the hydroxylation reaction of benzene to phenol with  $\text{H}_2\text{O}_2$ , while the selectivity of hydroxylation to phenol is still up to 99%. Although the conversion of benzene to phenol gradually decreases during the repeated use (three times), it is still a good catalyst during the reused process. The FT-IR spectra of initial and recycled CN-PMoV<sub>2</sub> are shown in Fig. 5 with lines 1, 2, 3, and 4 expressing the first, second, third, and fourth use, respectively. Based on the above experiment results, we speculate that PMoV<sub>2</sub> adsorption on the surface of g-C<sub>3</sub>N<sub>4</sub> is not very strong, and that acidic, heated conditions or strong stirring facilitate the shedding of catalytically active substances.

### Possible mechanism

The reaction mechanism for this reaction is suggested based on reported procedure [28, 36]. In this reaction system, benzene and hydrogen peroxide are respectively contacted with the heteropoly compound, which is adsorbed on the surface of the supporter. During this process, the benzene structure is activated to cause cleavage



**Fig. 5** FT-IR spectra of initial and recycled catalyst



**Fig. 6** A possible catalysis mechanism by CN-PMoV<sub>2</sub>

of the C–H bond; at the same time, pentavalent vanadium is reduced to tetravalent valence. In a corresponding process, tetravalent vanadium is oxidized to pentavalent vanadium by hydrogen peroxide under acidic conditions. Cross-conversion of tetravalent vanadium and pentavalent vanadium through electron transfer achieved sustained catalytic effect [30, 38] (Fig. 6).

## Conclusions

In conclusion, the vanadium-substituted phosphomolybdic heteropoly acid sodium salt immobilized on  $C_3N_4$  (CN-PMoV<sub>2</sub>) provided a satisfactory catalytic effect for hydroxylation of benzene to phenol. Under optimal reaction conditions [benzene (1.00 mL, 11.22 mmol), hydrogen peroxide (30 wt%, 3.40 mL, 33.90 mmol), acetonitrile (5.00 mL), acetic acid (5.00 mL), catalyst (100 mg), 80 °C, 20 h], the yield of phenol is more than 38.0% and the selectivity is up to 99.1%. As a heterogeneous catalytic system in this subject, the catalyst is easily recycled and still exhibits some certain catalytic effect even after three repeated uses.

## References

1. X. Gao, X. Lv, J. Xu, *Kinet. Catal.* **51**, 394 (2010)
2. I. Spiridon, R. Bodirlau, C.-A. Teaca, *Open. Life Sci.* **6**, 388–396 (2011)
3. T.B. İyim, I. Acar, S. Özgümiş, *J. Appl. Polym. Sci.* **109**, 2774 (2008)
4. M. Wang, M. Leitch, C.C. Xu, *J. Ind. Eng. Chem.* **15**, 870 (2009)
5. C.A. Antonyraj, K. Srinivasan, *Catal. Surv. Asia* **17**, 47 (2013)
6. A. Tabler, A. Häusser, E. Roduner, *J. Mol. Catal. A: Chem.* **379**, 139 (2013)
7. J.Z.X. Chen, X. Fu, M. Antonietti, X. Wang, *J. Am. Chem. Soc.* **21**, 11658 (2009)
8. M.M.Y. Ide, M. Ogawa, *J. Am. Chem. Soc.* **21**, 16762 (2010)
9. B. Lee, H. Naito, T. Hibino, *Angew. Chem. Int. Ed.* **51**, 440 (2012)
10. S.V.T. Punniyamurthy, Javed Iqbal, *Chem. Rev.* **9**, 2329 (2005)
11. K. Ohkubo, T. Kobayashi, S. Fukuzumi, *Angew. Chem. Int. Ed. Engl.* **50**, 8652 (2011)
12. X. Cai, Q. Wang, Y. Liu, J. Xie, Z. Long, Y. Zhou, J. Wang, *ACS Sustain. Chem. Eng.* **4**, 4986 (2016)
13. P.M.R.K. Asim Bhaumik, *J. Catal.* **178**, 101 (1998)
14. P.M. Rajiv Kumar, A. Bhaumik, *Catal. Today* **49**, 185 (1999)
15. Y.-Y. Gu, X.-H. Zhao, G.-R. Zhang, H.-M. Ding, Y.-K. Shan, *Appl. Catal. A* **328**, 150 (2007)
16. S.I. Niwa, *Science* **295**, 105 (2002)
17. M. Tani, T. Sakamoto, S. Mita, S. Sakaguchi, Y. Ishii, *Angew. Chem. Int. Ed.* **44**, 2586 (2005)
18. A. Kubacka, Z. Wang, B. Sulikowski, V. Cortescorberan, *J. Catal.* **250**, 184 (2007)
19. Y. Guo, X. Zhang, H. Zou, H. Liu, J. Wang, K.L. Yeung, *Chem. Commun.* **141**, 5898 (2009)
20. J. Chen, S. Gao, J. Xu, *Catal. Commun.* **9**, 728 (2008)
21. H. Yang, J.-Q. Chen, J. Li, Y. Lv, S. Gao, *Appl. Catal. A* **415–416**, 22 (2012)
22. K. Sun, H. Xia, Z. Feng, R. Vansanten, E. Hensen, C. Li, *J. Catal.* **254**, 383 (2008)
23. A. Wclaw, K. Nowińska, W. Schwieger, *Appl. Catal. A* **270**, 151 (2004)
24. M. Rivallan, G. Ricchiardi, S. Bordiga, A. Zecchina, *J. Catal.* **264**, 104 (2009)
25. G. Ding, W. Wang, T. Jiang, B. Han, H. Fan, G. Yang, *ChemCatChem* **5**, 192 (2013)
26. L. Balducci, D. Bianchi, R. Bortolo, R. D'Aloisio, M. Ricci, R. Tassinari, R. Ungarelli, *Angew. Chem.* **115**, 5087 (2003)
27. K.M. Parida, D. Rath, *Appl. Catal. A* **321**, 101 (2007)
28. P. Borah, X. Ma, K.T. Nguyen, Y. Zhao, *Angew. Chem. Int. Ed. Engl.* **51**, 7756 (2012)
29. Y. Zhou, G. Chen, Z. Long, J. Wang, *RSC Adv.* **4**, 42092 (2014)
30. B.B. Sarma, R. Carmieli, A. Collauto, I. Efremenko, J.M.L. Martin, R. Neumann, *ACS Catal.* **6**, 6403 (2016)
31. Z. Long, Y. Zhou, G. Chen, W. Ge, J. Wang, *Sci. Rep.* **4**, 3651 (2014)
32. P. Zhao, Y. Leng, M. Zhang, J. Wang, Y. Wu, J. Huang, *Chem. Commun. (Camb.)* **48**, 5721 (2012)
33. Z.W.Y. Li, R. Chen, Y. Wang, W. Xing, J. Wang, J. Huang, *Catal. Commun.* **122**, 1622 (2014)

34. Y. Zhao, R. Tang, R. Huang, *Catal. Lett.* **145**, 1961 (2015)
35. Y. Leng, J. Liu, P. Jiang, J. Wang, *Catal. Commun.* **40**, 84 (2013)
36. P. Zhao, Y. Leng, J. Wang, *Chem. Eng. J.* **204–206**, 72 (2012)
37. J.-S. Choi, S.-S. Yoon, S.-H. Jang, W.-S. Ahn, *Catal. Today* **111**, 280 (2006)
38. P. Borah, X. Ma, K.T. Nguyen, Y. Zhao, *Angew. Chem. Int. Ed.* **51**, 7756 (2012)