



Liquid phase hydroxylation of benzene to phenol over vanadium substituted Keggin anion supported on amine functionalized SBA-15

Ali Nemati Kharat*, Sayedreza Moosavikia, Bahareh Tamaddoni Jahromi, Alireza Badiei

School of chemistry, University College of science, University of Tehran, P.O. Box 13145-1357, Tehran, Iran

ARTICLE INFO

Article history:

Received 29 January 2011

Received in revised form 24 July 2011

Accepted 26 July 2011

Available online 4 August 2011

Keywords:

Modified SBA-15

Molybdovanadophosphoric acid

Hydroxylation

Phenol

Benzene oxidation

ABSTRACT

The Keggin type vanadium substituted molybdophosphoric acid ($H_5PMo_{10}V_2O_{40}$) supported on amine functionalized SBA-15 was tested in direct hydroxylation of benzene to phenol in the liquid phase. The catalyst was characterized by various techniques such as X-ray diffraction, FT-IR spectroscopy, thermogravimetric analysis (TGA), N_2 absorption-desorption surface area measurement and SEM. Gas chromatography of products showed high catalytic activity and selectivity to phenol. As we expected, the leaching of heteropoly acid from support during the reaction was negligible, because of strong interaction between heteropoly acid and amine groups of surface. The influence of reaction temperature, reaction time, amount of catalyst and H_2O_2 were investigated. Under optimized conditions 20% conversion of benzene and 95% selectivity to phenol was achieved.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Phenol is one of the most useful intermediates in manufacture of petrochemical, agrochemical and plastics [1–3]. It is also an essential chemical to produce phenolic resins and bisphenol A [4]. Currently, phenol is chiefly produced by three step Huck process that suffers from many disadvantages such as low yield, high energy consumption and production of acetone as byproduct [5]. In two past decades many endeavors were carried out to find one step procedure for the production of phenol by direct hydroxylation of benzene in liquid or gas phase. Owing to environmental and economical aspects, the use of molecular oxygen and hydrogen peroxide is preferred to other oxidants [6,7]. Hydrogen peroxide in comparison with oxygen shows more activity and better selectivity. In spite of its advantages, hydrogen peroxide is inherently corrosive and tends to catalytic decomposition in high concentration. In order to overcome these significant drawbacks usually diluted aqueous solution is used, however the excess water often produces a biphasic mixture and leads to separation of organic substrate and active catalyst species [8,9]. It is worth mentioning that the reaction of hydrogen peroxide with aromatic compounds proceeds in the presence of transition metal ions of different oxidation states [10,11]. Polyoxometalates belong to a large class of nano-sized metal–oxygen clusters. Generally there are two kind of polyoxometalates based on their chemical composition:

heteropoly and isopoly anions that the former is more active for catalytic applications [12]. Molybdenum (VI) and tungsten (VI) are the best polyoxometalates formers as the result of their favorable combination of ionic radius, charge and accessibility of empty d orbitals for metal–oxygen π bonding [13]. Heteropoly compounds with their redox and acidic properties are active catalysts for various oxidation reactions [14–17]. In addition, heteropoly compounds have inherent stability toward oxygen donors such as molecular oxygen and hydrogen peroxide, therefore they are useful catalysts for liquid phase oxidation [18]. The main drawback for heteropoly anions catalytic application is their low specific area, hence for many applications, heteropoly compounds are dispersed on a high surface area carriers [19,20]. The result of direct dispersion of HPAs on a conventional supports such as silica, TiO_2 , carbon, or Al_2O_3 show that anchoring HPA on the surface of these supports is not stable and the loaded HPAs can be easily released by polar solvents resulting in the leaching of the active site from the supports. To minimize this problem, modification by silanization has been explored to bind heteropoly acids on the surface of support and an acid–base interaction made has been invoked to explain their interaction [21].

Here, in this work we synthesized the vanadium-substituted heteropoly acid ($H_5PMo_{10}V_2O_{40} \cdot nH_2O$) and loaded this HPA on amine functionalized SBA-15. This catalyst was tested in direct hydroxylation of benzene to phenol and the optimum conditions were investigated. In order to show the influence of silanization, the activity of this catalyst was compared with loaded HPAs according to impregnation method over conventional supports such as NaY and MCM-41.

* Corresponding author. Tel.: +98 21 61112499; fax: +98 21 66495291.
E-mail address: alnema@khayam.ut.ac.ir (A. Nemati Kharat).

2. Experimental

2.1. Materials

The polyoxometalates used in this work, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$, were synthesized in our laboratory with literature methods [12,22]. Triblock copolymer poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (P123), tetraethyl orthosilicate (TEOS), hydrochloric acid (37%), 3-aminopropyltriethoxysilane (APTES), molybdenum trioxide, vanadium pentoxide, phosphoric acid 85%, acetonitrile, benzene, hydrogen peroxide (30%) and toluene were purchased from Merck.

2.2. Synthesis of SBA-15

The synthesis of SBA-15 was carried out according to zhao's method [23]. Typically, 4 g of triblock copolymer P123 was dissolved in 30 g deionized water and 120 ml of HCl 2 M solution with constant stirring while temperature was kept at 40 °C. After that, 8.5 g of TEOS was added during 30 min and the resulting mixture was stirred at 40 °C for 24 h. In the last step, the mixture was aged for 48 h at 100 °C under static condition. The white solid was filtered, washed with warm water, dried in room temperature, and calcined in air at 550 °C for 5 h.

2.3. Preparation of amino-functionalized SBA-15

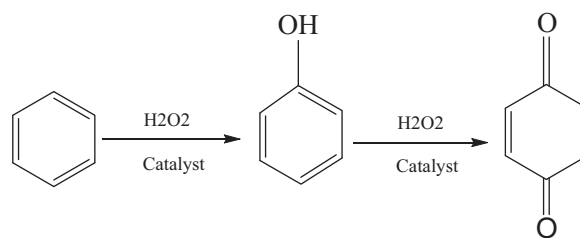
Amine modification of SBA-15 was performed according to reported procedure [24]. In a typical preparation 2 g SBA-15 was heated up to 110 °C under vacuum and immediately was dispersed in 50 ml dried toluene and was refluxed for 4 h to remove the occupied moisture. 1 g APTES was dissolved in 10 ml toluene and was added dropwise to above suspension and was refluxed for another 4 h. The mixture was cooled to room temperature and the solid was filtered. The resulting solid was washed three times with warm ethanol to remove unreacted APTES and then was dried at room temperature. The product is designated as NH_2 -SBA-15.

2.4. Synthesis of di-vanadium substituted molybdovanadophosphoric acid

Vanadium substituted molybdophosphoric acid ($\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}\cdot x\text{H}_2\text{O}$) was synthesized at the P/V/Mo molar ratio of 1/2/10 using MoO_3 , V_2O_5 and H_3PO_4 85% [22]. 9.6 g, 66.7 mmol MoO_3 , and 1.214 g, 6.67 mmol V_2O_5 were dispersed in 150 ml deionized water in a 500-ml three-necked glass flask equipped with a condenser and magnetic bar. The suspension was heated to reflux temperature using an oil bath. 1.15 g, 6.67 mmol 85% H_3PO_4 , was added dropwise to the suspension. The above mixture was maintained at 120 °C and stirred for 24 h, dark suspension turned to a clear orange–red solution. The solvent was evaporated to yield a solid product.

2.5. Anchoring of molybdovanadophosphoric acid onto NH_2 -SBA-15

0.1 g of molybdovanadophosphoric acid (HPMoV) was dissolved in 50 ml acetonitrile and then 0.9 g NH_2 -SBA-15 was dispersed in above solution and refluxed for 4 h. The product was filtered, washed with acetonitrile and then dried at 100 °C under vacuum. The final product is designated as HPMoV/ NH_2 -SBA-15. This catalyst was used in hydroxylation of benzene to phenol and its activity was compared with impregnated HPAs on HY and MCM-41. For impregnation, typically 0.1 g HPMoV dissolved in 1:1 deionized water–ethanol solution and then 0.9 g support (HY or MCM-41) was added and the resulting suspension was stirred for 24 h at



Scheme 1. The hydroxylation reaction of benzene.

room temperature. The solid product obtained after evaporation of solvent dried at 110 °C for 12 h.

2.6. Catalytic test

All reactions were carried out in three neck 50 ml flask equipped with a magnetic stirring bar and reflux condenser. Typically 0.1 g catalyst was dispersed in 6 ml acetonitrile. When reaction temperature was fixed, 1 ml benzene and desired amount of hydrogen peroxide 30% was added to the suspension. The mixture was stirred constantly at the required temperature for 1–8 h. Conversions and selectivities were calculated by gas chromatography using toluene as internal standard. Under this condition in addition to phenol as main product, 1,4-benzoquinone was detected as byproduct (Scheme 1)

$$\text{Conversion of benzene} = \frac{\text{mmol phenol} + \text{mmol benzoquinone}}{\text{mmol initial benzene}}$$

$$\begin{aligned} \text{Selectivity to phenol(1, 4-benzoquinone)} \\ = \frac{\text{mmol phenol(1, 4-benzoquinone)}}{\text{mmol phenol} + \text{mmol benzoquinone}} \end{aligned}$$

2.7. Apparatus and instruments

X-ray pattern was obtained on a Bruker AXSD8 diffractometer at $2\theta = 1\text{--}10^\circ$ with Ni filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) operated at 40 kV and 30 mA. N_2 adsorption–desorption isotherms were obtained using BELSORP-mini II at 77 K. SBA-15, NH_2 -SBA-15 and NH_2 -SBA-15 were degassed at 200 °C, 100 °C and 100 °C respectively for 3 h. The specific surface areas were calculated with Brunauer–Emmett–Teller (BET) equation and Barret–Joyner–Halenda (BJH) method was used for computing the pore size distribution and total pore volume. V and Mo contents were determined by ICP using varian VISTA-MPX model. The FT-IR spectra for the powdered samples were obtained over a range of 600–4000 cm^{-1} on a EQUINOX 55BRUKER. Thermal gravimetric analysis (TGA) was conducted on a TGA Q50 V6.3. Sample sizes of 11.929 and 4.626 mg were used for HPMoV, and NH_2 -SBA-15, respectively. The SEM images of SBA-15, NH_2 -SBA-15 and HPMoV/ NH_2 -SBA-15 were obtained using Philips XL30.

3. Result and discussion

3.1. Catalyst characterization

The XRD patterns for SBA-15 and HPMoV/ NH_2 -SBA-15 were illustrated in Fig. 1. Three reflections, one strong in 2θ less than 1 and two in 2θ 1.6 and 1.8 with lower intensity attributed to (1 0 0), (1 1 0) and (2 0 0) planes are all well consistent with hexagonal pore arrays. The diffraction patterns indicate that the primary structure of SBA-15 are maintained after modification with APTES

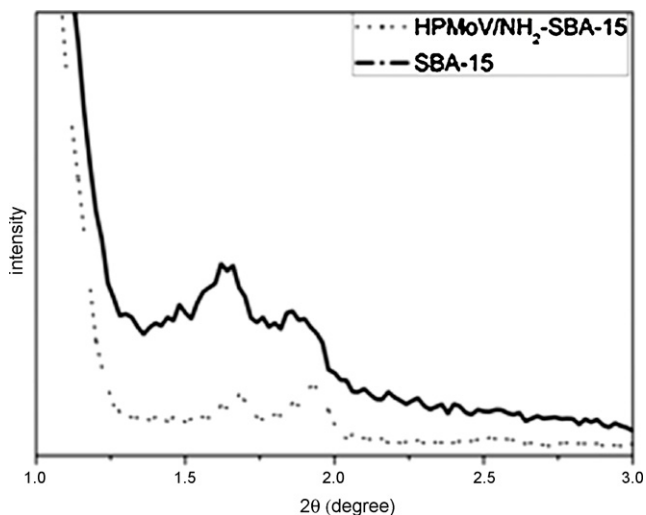


Fig. 1. The XRD patterns of SBA-15 and NH_2 -SBA-15-HPMoV.

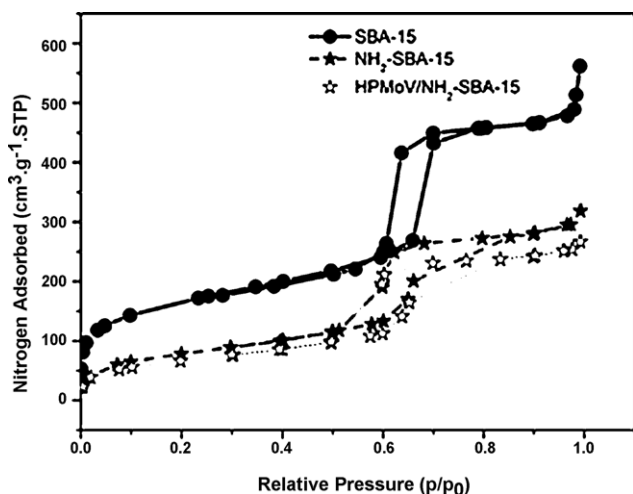


Fig. 2. Adsorption–desorption isotherms of SBA-15, NH_2 -SBA-15 and HPMoV/ NH_2 -SBA-15.

and anchoring with HPMoV. As we can see the reflections of modified sample is reduced in intensity and as a result we can conclude that the modification of SBA-15 with APTES and anchoring with HPMoV occurred in the pores of SBA-15.

Nitrogen adsorption–desorption for SBA-15, NH_2 -SBA-15 and HPMoV/ NH_2 -SBA-15 were performed by BET method at 77 K and resultant isotherms are depicted in Fig. 2. Isotherm curves for all samples exhibit a type IV isotherms which indicate all samples have well ordered mesoporous structure. The textural properties of samples including specific surface area, pore diameter and total pore volume are given in Table 1. Because of modification of SBA-15 with APTES, a reduction in specific surface area from 554 to 281 m^2/g can be seen, and also loading this catalyst with heteropoly acid leads

Table 1

The specific surface area (S_{BET}), pore diameter and total pore volume of SBA-15, NH_2 -SBA-15 and HPMoV/ NH_2 -SBA-15.

Samples	S_{BET} (m^2/g)	Pore diameter (nm)	Total pore volume (cm^3/g)
SBA-15	554.03	6.18	0.8586
NH_2 -SBA-15	281.32	6.18	0.4884
HPMoV/ NH_2 -SBA-15	237.43	5.42	0.4097

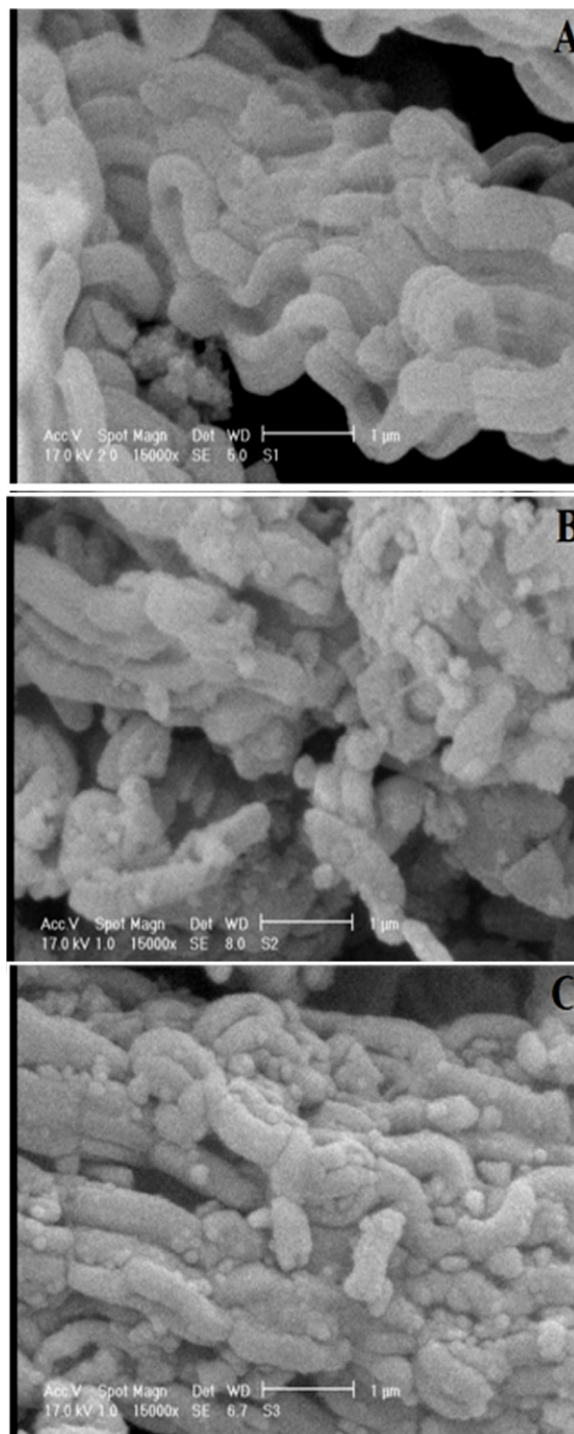


Fig. 3. SEM images of the (A) SBA-15, (B) NH_2 -SBA-15 and (C) HPMoV/ NH_2 -SBA-15.

to more reduction in specific surface area. Similarly same behavior are expected for pore diameter and total pore volume.

The SEM images for SBA-15, NH_2 -SBA-15 and HPMoV/ NH_2 -SBA-15 are shown in Fig. 3. All samples show robe-like structure which is well consistent with known SBA-15 structure [25,26]. SEM image also provides evidence for the structural integrity of SBA-15, NH_2 -SBA-15 and HPMoV/ NH_2 -SBA-15. We can infer that functionalization with APTES and anchoring with HPMoV have no strong effect on pure SBA-15.

Fig. 4 shows the FT-IR spectroscopy of $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$, NH_2 -SBA-15 and HPMoV/ NH_2 -SBA-15. The Keggin type heteropoly acid

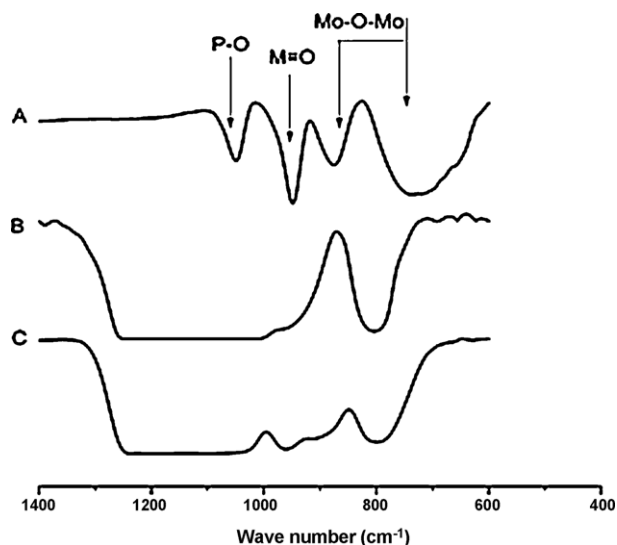


Fig. 4. FT-IR spectrum of (A) HPMoV, (B) NH_2 -SBA-15 and (C) HPMoV/ NH_2 -SBA-15.

has four characteristic peaks in range of $750\text{--}1100\text{ cm}^{-1}$ [27]. It can be seen that peaks appeared at 734 cm^{-1} and 875 cm^{-1} correspond to Mo–O–Mo and at 948 cm^{-1} and 1049 cm^{-1} are related to M=O and P–O that explicitly indicates the neat structure of Keggin type heteropoly acid. In FT IR spectrum of HPMoV/ NH_2 -SBA-15 these peaks overlaps with NH_2 -SBA-15, therefore these information cannot confirm that loading of heteropoly acid was occurred over NH_2 -SBA-15. However due to appearance of two new peaks in FT-IR spectrum of HPMoV/ NH_2 -SBA-15 in range of $850\text{--}950\text{ cm}^{-1}$ in comparison with NH_2 -SBA-15 it can induce that HPMoV actually exists in the pores of NH_2 -SBA-15.

Purity of synthesized heteropoly acid was confirmed by measuring Mo/V molar ratio by ICP. Fig. 5(A) represents the thermogravimetric analysis of HPMoV that shows mass loss up to 150°C which is related to physically absorbed water. This amount of mass loss, 10.38%, is related to 11.12 H_2O per Keggin unit. The mass loss from 180 to 450°C is related to decomposition of HPMoV to corresponding oxides. Also in order to determine the value of reacted APTES, thermal gravimetric analysis was applied. Fig. 5(B) shows the TGA profile for NH_2 -SBA-15. The mass loss in range of $100\text{--}600^\circ\text{C}$ is attributed to removal of carbon chain and NH_2 group. The mass loss due to organic compounds was 6.8867% of the initial mass, therefore the amount of NH_2 was determined 1.2 mmol.

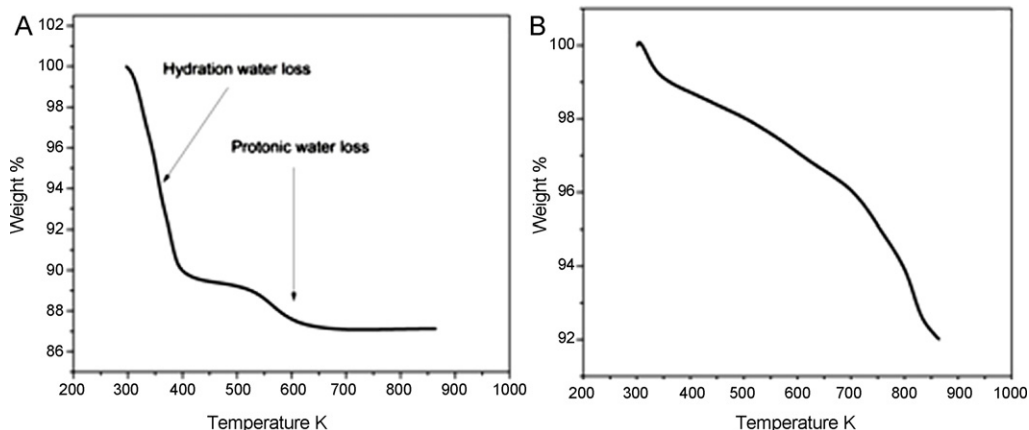


Fig. 5. Thermal gravimetric analysis of (A) HPMoV and (B) NH_2 -SBA-15.

3.2. Catalyst performance

The catalytic activity of HPMoV supported on Amine functionalized SBA-15 was tested in direct hydroxylation of benzene in acetonitrile as solvent and the results were shown in Table 2. The activity of supported HPMoV were compared with unsupported HPMoV and HPMo. Also in order to show the effect of modification on the leaching supports the activity of HPMoV/ NH_2 -SBA-15 was compared with HPMoV/HY and HPMoV/MCM-41.

As can be seen, pure HY, MCM-41 and SBA-15 show no activity in conversion of benzene to phenol and also it is clear that HPMo has no activity in this particular reaction (see run 1–4). By comparison of run 4 with run 5, we concluded that vanadium species are active species in this reaction. Comparison 6 with 7 and 8 with 9 lead us that molybdovanadophosphoric acid leached from HY and MCM-41 but the values of benzene conversion in run 10 and 11 expressed that no leaching has occurred when functionalized support is used. Therefore it was chosen as desirable catalyst and reaction conditions, such as reaction temperature, reaction time, amount of catalyst and H_2O_2 were investigated for this catalyst.

3.3. Effect of reaction temperature

In order to investigate the effect of temperature on the catalytic activity, several discrete reactions was carried out under the same reaction conditions and the results are depicted in Fig. 6. In low temperatures phenol was detected as the only product. Increasing in reaction temperature leads to decrease in selectivity toward phenol. This reduction in selectivity is related to further oxidation of phenol at higher temperature. As illustrated in Fig. 6 increase in the conversion of benzene was observed along with increase in temperature up to 60°C , and then, decrease in benzene conversion, with further increase in reaction temperature was observed, this decrease is probably because of two reasons, first, the spontaneous decomposition of H_2O_2 to O_2 at high temperatures [28] and second, an alteration in active species [29–32].

Previous reports manifestly explained that vanadic oxide species (VO_2^+) detach from the Keggin unit at high temperatures. The presence of these species were well proved by carrying out ^{51}V NMR, ^{31}P NMR and FT-IR spectroscopy for catalysts before and after reaction and have proved that this species are responsible for the deactivation of recovered HPMoV for the phenol formation [31]. Both of two mentioned factors are responsible for reduction in benzene conversion in high temperatures. According to what men-

Table 2
Direct oxidation of benzene to phenol with aqueous hydrogen peroxide using different catalysts.^a

Selective conversion of H ₂ O ₂	Selectivity to banzoquinone	Selectivity to phenol	Benzene conversion%	Catalyst	Run
–	–	–	0	HY	1
–	–	–	0	SBA-15	2
–	–	–	0	MCM-41	3
–	–	–	0	H ₅ PMo ₁₂ O ₄₀	4
10.3	8	92	25.4	(HPMoV) H ₅ PMo ₁₀ V ₂ O ₄₀	5
9.00	7	93	22	HY/HPMoV	6
2.00	5	95	5	HY ^b /HPMoV	7
8.16	7	93	20	MCM-41/HPMoV	8
4.80	7	93	11	MCM-41 ^b /HPMoV	9
8.03	5	95	20	NH ₂ -SBA-15/HPMoV	10
7.63	5	95	19	NH ₂ -SBA-15 ^b /HPMoV	11

^a Reaction conditions: 1 ml benzene, 3 ml 30% H₂O₂, 6 ml acetonitrile, 0.1 g. HPMoV/NH₂-SBA-15, temperature 60 °C, reaction time 6 h.

^b Reuse of the catalyst after separation from the reaction mixture.

tioned above and (Fig. 6), 60 °C is considered as a optimum reaction temperature.

3.4. Effects of reaction time

The influence of reaction time in hydroxylation of benzene in 60 °C was investigated by several separate reaction under the same reaction conditions and results are depicted in Fig. 7. It can be observed that the conversion of benzene increases along with expansion the reaction time up to 8 h, Benzene conversion was not affected by further increasing in temperature and reached a plateau in the reaction period of 8–9 h; however, the selectivity to phenol decreased with reaction time due to further oxidation of phenol. The suitable reaction time for oxidation of benzene, was found to be 6 h.

3.5. Effect of the amount of H₂O₂

The impact of the amount of H₂O₂ on the hydroxylation of benzene was investigated and results are portrayed in Fig. 8. It is seen that the conversion of benzene increased while the amount of H₂O₂ increased and also it is observed that the selectivity toward phenol decreased when more than 3 ml H₂O₂ (molar ratio H₂O₂ to benzene equals to 2.6) was employed which is due to further oxidation of phenol. Stoichiometrically in oxidation of benzene to phenol, the molar ratio of H₂O₂ to benzene is 1:1, but because of spontaneous decomposition of hydrogen peroxide, in practice, we needed

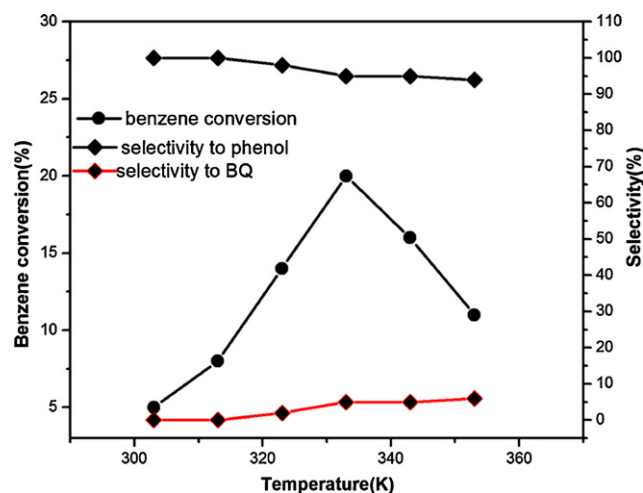


Fig. 6. Effect of reaction temperature on the conversion of benzene and selectivity to phenol using HPMoV/NH₂-SBA-15^a. ^aReaction conditions: 1 ml benzene, 3 ml 30% H₂O₂, 6 ml acetonitrile, 0.1 g. HPMoV/NH₂-SBA-15, reaction time 6 h.

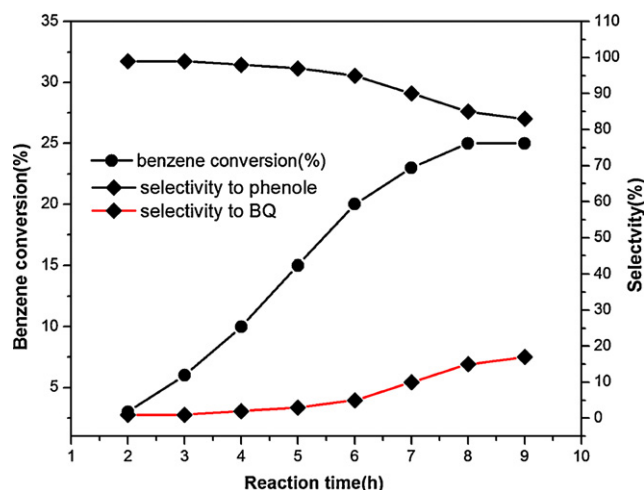


Fig. 7. Effect of reaction time on the conversion of benzene and selectivity to phenol using HPMoV/NH₂-SBA-15^a. ^aReaction conditions: 1 ml benzene, 3 ml 30% H₂O₂, 6 ml acetonitrile, HPMoV/NH₂-SBA-15, reaction temperature 60 °C.

2.6 times more stoichiometric volume. In fact, in the reaction of benzene hydroxylation, the amount of consumed hydrogen peroxide by self-decomposition is much more than that of consumed in the hydroxylation reaction [29] and this may provide some under-

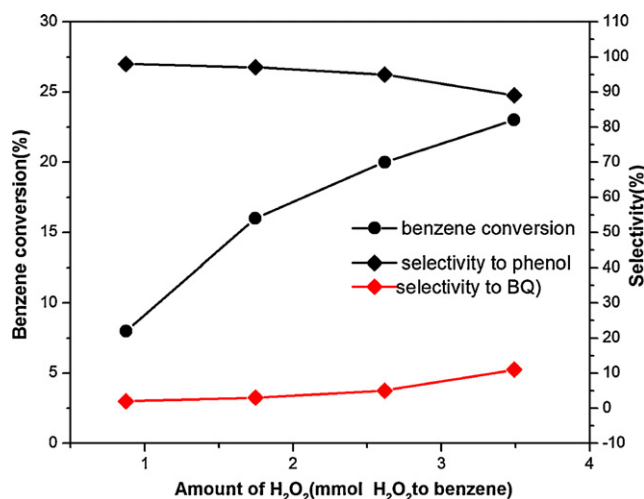


Fig. 8. Effect of the amount of hydrogen peroxide on the conversion of benzene and selectivity to phenol using HPMoV/NH₂-SBA-15^a. ^aReaction conditions: 1 ml benzene, 6 ml acetonitrile, 0.1 g HPMoV/NH₂-SBA-15, reaction temperature 333 K, reaction time 6 h.

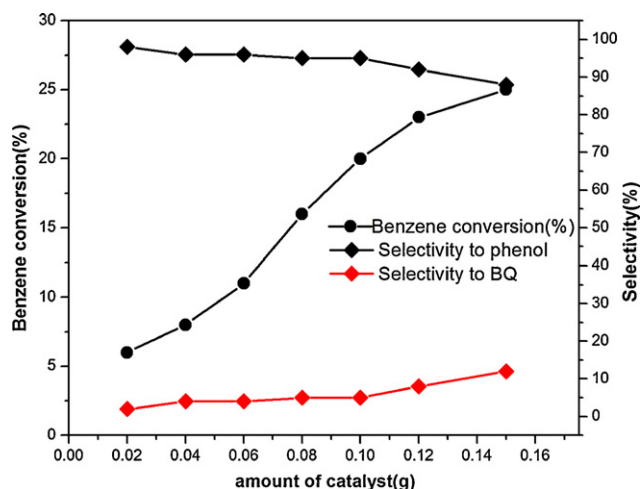


Fig. 9. Effect of the amount of catalyst on the conversion of benzene and selectivity to phenol using HPMoV/NH₂-SBA-15^a. ^aReaction conditions: 1 ml benzene, 3 ml 30% aq. H₂O₂, 6 ml acetonitrile, reaction temperature 333 K, reaction time 6 h.

standings for the very low selective conversion of H₂O₂ shown in Table 2. It was determined that 3 ml 30% aq. H₂O₂ is appropriate volume in this reaction.

3.6. Effect of the amount of catalyst

In order to investigate the influence of the amount of catalyst several experiments were set up in range 0.02–0.16 g catalyst and the results are reflected in Fig. 9. As we can see, the conversion of benzene increased from 6% to 25% corresponding to low and high limits. The selectivity to phenol decreased sharply when more than 0.1 g catalyst was used, and this could be attributed to further oxidation of phenol. Therefore, 0.1 g catalyst was found to be optimum amount of catalyst for hydroxylation of benzene to phenol.

3.7. Stability investigation of catalyst

In order to investigation of catalyst stability, vanadium substituted Keggin anion supported on amine functionalized SBA-15, was reused several times. After each run, the catalyst was separated by centrifuge, washed with acetonitrile and used for the next run. After the fifth run, the conversion of benzene decreased to 15% (equal to 75% activity of the fresh catalyst). As mentioned VO₂⁺ species can be segregate from Keggin unit and led to reduction in catalyst activity.

4. Conclusion

In this work, we prepared molybdophosphoric acid containing vanadium supported on amine functionalized SBA-15 and employed this catalyst for direct hydroxylation of benzene to phenol in acetonitrile medium. This catalyst shows good activity in this reaction, in addition owing to strong acid–base interaction between heteropoly anions and amine group it exhibits good stability against leaching. It is found that vanadium species are active sites in this certain reaction.

References

- [1] J. Zhang, Y. Tang, G. Li, C. Hu, *Appl. Catal. A: Gen.* 278 (2005) 251–261.
- [2] K. Lemke, H. Ehrich, U. Lohse, H. Berndt, K. Jähnisch, *Appl. Catal. A: Gen.* 243 (2003) 41–51.
- [3] M. Stöckmann, et al., *Appl. Catal. A: Gen.* 208 (2001) 343–358.
- [4] S. Sumimoto, et al., *Ind. Eng. Chem. Res.* 45 (2006) 7444–7450.
- [5] S.I. Niwa, et al., *Science* 295 (2002) 105–107.
- [6] L.C. Passoni, F.J. Luna, M. Wallau, R. Buffon, U. Schuchardt, *J. Mol. Catal. A: Chem.* 134 (1998) 229–235.
- [7] M. Jian, et al., *J. Mol. Catal. A: Chem.* 253 (2006) 1–7.
- [8] G. Strukul, *Angew. Chem. Int. Ed.* 37 (1998) 1198–1209.
- [9] J.E. Remias, T.A. Pavlosky, A. Sen, *J. Mol. Catal. A: Chem.* 203 (2003) 179–192.
- [10] N.I. Kuznetsova, N.V. Kirillova, L.I. Kuznetsova, M.Y. Smirnova, V.A. Likhohobov, *J. Hazard. Mater.* 146 (2007) 569–576.
- [11] K. Nomiya, S. Matsuoka, T. Hasegawa, Y. Nemoto, *J. Mol. Catal. A: Chem.* 156 (2000) 143–152.
- [12] I. Kozhevnikov, *Catalysts for Fine Chemical Synthesis: Catalysis by Polyoxametalate*, Wiley & Sons, England, 2002.
- [13] J.B. Moffat, in: M.V. Twigg, M.S. Spencer (Eds.), *Metal–Oxygen Clusters, The Surface and Catalytic Properties of Heteropoly Oxometalates*, Kluwer Academic Publisher, New York, 2000.
- [14] N. Mizuno, M. Misono, *Chem. Rev.* 98 (1998) 199–218.
- [15] I.A. Weinstock, *Chem. Rev.* 98 (1998) 113–170.
- [16] R. Neumann, A.M. Khenkin, *Chem. Commun.* (2006) 2529–2538.
- [17] M. Misono, *Chem. Commun.* (2001) 1141–1152.
- [18] H. Ge, et al., *Sci. China Ser. B: Chem.* 52 (2009) 1264–1269.
- [19] H.L. Li, et al., *Langmuir* 19 (2003) 10409–10413.
- [20] I.V. Kozhevnikov, *Appl. Catal. A: Gen.* 256 (2003) 3–18.
- [21] M. Kamada, H. Kominami, Y. Kera, *J. Colloid Interface Sci.* 182 (1996) 297–300.
- [22] B.B. Bardin, R.J. Davis, *Appl. Catal. A: Gen.* 185 (1999) 283–292.
- [23] D. Zhao, et al., *Science* 279 (1998) 548–552.
- [24] N.K.K. Raj, S.S. Deshpande, R.H. Ingle, T. Raja, P. Manikandan, *Catal. Lett.* 98 (2004) 217–223.
- [25] A. Lapkin, et al., *Catal. Today* 81 (2003) 611–621.
- [26] S. Che, et al., *Angew. Chem. Int. Ed.* 42 (2003) 2182–2185.
- [27] H. Ge, Y. Leng, C. Zhou, J. Wang, *Catal. Lett.* 124 (2008) 324–329.
- [28] P. Chammingkwan, W.F. Hoelderich, T. Mongkhonsi, P. Kanchanawanichakul, *Appl. Catal. A: Gen.* 352 (2009) 1–9.
- [29] Y. Leng, H. Ge, C. Zhou, J. Wang, *Chem. Eng. J.* 145 (2008) 335–339.
- [30] Y. Tang, J. Zhang, *Trans. Met. Chem.* 31 (2006) 299–305.
- [31] S.T. Yamaguchi, S. Sumimoto, Y. Ichihashi, S. Nishiyama, S. Tsuruya, *Ind. Eng. Chem. Res.* 44 (2005) 1–7.
- [32] N.A. Alekar, et al., *J. Mol. Catal. A: Chem.* 164 (2000) 181–189.