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Keggin 型杂多酸铯盐催化苯羟基化反应

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摘要　采用室温固相法制备了具有 Keggin 结构的杂多酸铯盐催化剂($Cs_xH_{3+n-x}PMo_{12-n}V_nO_{40}$, n=0, 1, 2, x=0.5～3.0). 红外、X 射线粉末衍射及循环伏安技术研究显示, 钒取代钼原子可提高催化剂的氧化还原性, 铯取代数的增加可提高催化剂的疏水性但降低氧化还原性. 在 H_2O_2 为氧化剂的苯羟基化反应中, 随着铯取代数目的增加, 催化剂的溶脱情况得到明显改善. 在氧化还原性和疏水性协同作用下, $Cs_2H_3PMo_{10}V_2O_{40}$ 在 $Cs_xH_{3+n-x}PMo_{12-n}V_nO_{40}$ 系列催化剂中显示出相对最佳的苯羟基化催化活性(苯酚收率 19.2%)和重复使用性能.

关键词　杂多酸; 铯盐; 苯; 羟基化; 苯酚

Catalytic Hydroxylation of Benzene to Phenol with Hydrogen Peroxide over Cesium Salts of Keggin-type Heteropoly Acids

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Abstract　Three series of cesium salts of Keggin-type heteropoly acids ($Cs_xH_{3+n-x}PMo_{12-n}V_nO_{40}$, n=0, 1, 2, x=0.5～3.0) prepared by a solid synthesis method have been employed in the catalytic hydroxylation of benzene to phenol with H_2O_2. The effects of vanadium substitution number and cesium content on the catalytic activity, redox ability and hydrophobicity of the catalysts were studied. $Cs_2H_3PMo_{10}V_2O_{40}$ exhibits high phenol yield (19.2%) and good reusability among the $Cs_xH_{3+n-x}PMo_{12-n}V_nO_{40}$ catalysts.

Keywords　heteropoly acid; cesium salt; benzene; hydroxylation; phenol

1　Introduction

Phenol is one of the most important intermediates in chemical industry. Currently, phenol is produced mainly through a multi-step process called the cumene process, which produces many byproducts. Thus, one-step process for the production of phenol by direct oxidation of benzene attracts much attention in the recent years.[1-9]

Heteropoly acids (HPAs) and their related compounds have been used as catalysts in many acid and redox reactions.[10-16] HPAs have several advantages as catalysts, *e.g.* they exhibit fast reversible multielectron transfer under rather mild conditions and their catalytic properties can be tuned by changing the identity of charge-compensating counter cations, heteroatoms, and addenda atoms. Classical Keggin-type HPAs are usually used as acid catalysts, however, a wide variety of transition metal-substituted heteropolyanions exhibit high catalytic activity in liquid phase oxidation reactions.[17] It was reported that partial substitution of Mo(VI) by V(V) in the $PMo_{12}O_{40}^{3-}$ anion would affect redox property and stability of the polyoxoanion, which improves the catalytic activity in hydroxylation of benzene[18] and oxidation of toluene.[19]

It is well known that the application of pure HPA catalysts is hampered by their low surface area and high solubility in polar media. These drawbacks can be overcome by partially exchanging protons of the parent HPAs with large cations, such as Cs^+, K^+, Rb^+ and NH_4^+ *etc.*, leading to the resulting compounds with better water-insolubility and higher surface area.[17] The pure and supported cesium salts of tungstophosphoric acid have been used in many liquid phase acid catalyzed reactions.[20,21] Okuhara *et al*. reported that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst could act as water-tolerant solid acid catalyst for the hydrolysis of ethyl acetate and the reaction rate of the 5th run was almost 90% that of the 1st run.[22] For oxidation reactions, cesium salts of Keggin-type polymolybdic acids were used for the gaseous phase selective oxidation

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of propane,[23] isobutane,[24] isobutyric acid[25] and benzene[26] owing to their oxidizing ability and high thermal stability. On the other hand, they were also used in some liquid phase oxidation reactions. Villabrille *et al.*[27] found that cesium salts of $H_4PMo_{11}VO_{40}$ showed high catalytic activity in liquid phase oxidation of 2,6-dimethylphenol to 2,6-dimethyl-*p*-benzoquinone with easy separation. Yamaguchi *et al.* reported the oxidation of benzene over the cesium salts of heteropoly acids ($CsPMoV_n$, n=1—3) using O_2 as oxidant.[28] Compared with the application of cesium salts of heteropoly acids as catalyst in acid reactions and gaseous phase oxidation reactions, their application in liquid phase oxidation reaction as water-tolerant catalysts was rare.[29-31]

From the synthetic point of view, the typical procedure for preparation of cesium salts of HPAs are generally proceeded through a solution method by titrating the controlled amount of an aqueous solution of Cs_2CO_3 into the aqueous solution of HPA.[32,33] In the previous report we found that the solid synthesis method by ball milling of HPA with $CsNO_3$ at room temperature is much simpler than the solution method, which is convenient to control the cesium content and has great potential in large scale preparation.[34]

In the present work, cesium salts of vanadium-substituted molybdophosphoric acid, $Cs_xH_{3+n-x}PMo_{12-n}V_nO_{40}$ (n=0, 1, 2, x=0.5—3.0), have been prepared by the solid synthesis method. The catalytic activity of these $Cs_xH_{3+n-x}PMo_{12-n}V_nO_{40}$ catalysts along with their corresponding pure HPAs was tested in the direct hydroxylation of benzene to phenol. The effects of vanadium substitution number and cesium content on the catalytic activity and redox ability of the catalysts were investigated. The leaching of heteropolyanion species and the reusability of the catalysts in repeating cycles were also studied.

2 Results and discussion

2.1 Characterization of the catalysts

^{31}P MAS NMR is normally used to check the purity of heteropoly acid, *e.g.* pure $H_5PMo_{10}V_2O_{40}$ shows five ^{31}P NMR peaks from its five geometrical isomers and pure $H_4PMo_{11}VO_{40}$ shows only one peak.[35] The heteropoly acids in this work were prepared with the conventional method[35,36] and their purities were proved by the ^{31}P MAS NMR.[35] The FT-IR bands of three heteropoly acids and $Cs_xH_{5-x}PMo_{10}V_2O_{40}$ catalysts in the range of 600—1300 cm^{-1} are shown in Figure 1. All samples show the characteristic IR bands of the Keggin unit. The asymmetric stretching of the central atom-oxygen (P—O) bond of PO_4 tetrahedron, ν_{as}(P—O_a), appears in the range of 1060—1065 cm^{-1}, while the asymmetric stretching of peripheral atom-terminal oxygen (M=O) bond, ν_{as}(M—O_d), appears in the range of 960—963 cm^{-1}. The inter-octahedral ν_{as}(M—O_b—M) and intra-octahedral ν_{as}(M—O_c—M) bands appear in the range of 864—870 cm^{-1} and 775—784 cm^{-1}, respectively.[37,38] Compared to the three pure heteropoly acids, above four characteristic IR bands shift to a lower wavenumber with incorporation of V^{5+} ion in the Keggin structure, which arises from the weaker interaction of V—O bond than that of Mo—O bond and the distortion

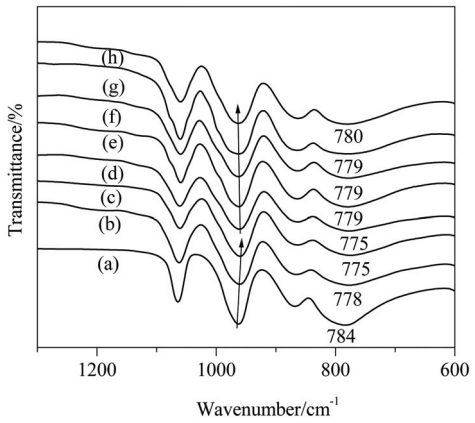

Figure 1 The FT-IR spectra of (a) $H_3PMo_{12}O_{40}$, (b) $H_4PMo_{11}VO_{40}$, (c) $H_5PMo_{10}V_2O_{40}$, (d) $Cs_{0.5}H_{4.5}PMo_{10}V_2O_{40}$, (e) $Cs_{1.2}H_{3.8}PMo_{10}V_2O_{40}$, (f) $Cs_2H_3PMo_{10}V_2O_{40}$, (g) $Cs_2H_3PMo_{10}V_2O_{40}$ after reaction and (h) $Cs_{2.5}H_{2.5}PMo_{10}V_2O_{40}$

of PO_4 tetrahedral environment in the Keggin structure upon substitution with vanadium.[27,39] Replacing proton by Cs^+ induces a slight shift in the ν_{as}(M—O_d) and ν_{as}(M—O_c—M) bands to higher wavenumber with gradually increasing cesium content. This shift is due to the strengthening of the M—O_d bond as the protonated water clusters are replaced by Cs^+.[40]

The XRD patterns in Figure 2 show that $H_5PMo_{10}V_2O_{40}$ belongs to triclinic crystal system. Partial replacement of proton by Cs^+ leads to the formation of cubic phase (*Pn*3*m*) which is commonly associated with the pure alkaline salts of heteropoly acids.[10,41,42] For the salts with composition of $Cs_{0.5}H_{4.5}PMo_{10}V_2O_{40}$, both triclinic and cubic phases exist, however, only the cubic phase forms for the salts with $x \geqslant 1$. The cubic unit cell increases with Cs^+ substitution number up to 1.5 and remains constant for higher Cs^+number (a=11.816 Å). The XRD patterns of $Cs_xH_{4-x}PMo_{11}VO_{40}$ show the similar trend with $Cs_xH_{5-x}PMo_{10}V_2O_{40}$. In addition, the molar ratios of Cs : P : Mo : V by ICP well correspond with the calculated values. Combined with the results from IR, XRD and ICP, the composition and structure of the catalysts are defined.

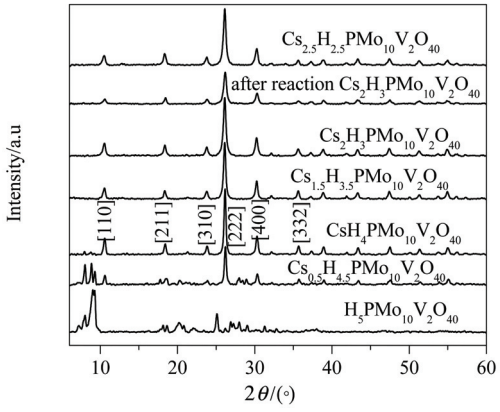

Figure 2 XRD patterns of $Cs_xH_{5-x}PMo_{10}V_2O_{40}$ catalysts

In order to investigate the redox properties of $Cs_xH_{3+n-x}PMo_{12-n}V_nO_{40}$ samples, they were used as modi-

fier to fabricate chemically modified carbon paste electrode (CPE). Figure 3A shows the cyclic voltammograms of $H_{3+n}PMo_{12-n}V_nO_{40}$-CPE and a new redox peak of I-I' appears at more positive potential position for $H_4PMo_{11}VO_{40}$ or $H_5PMo_{10}V_2O_{40}$ compared with that of $H_3PMo_{12}O_{40}$, which is attributed to the reversible redox process of vanadium.[43] Three other redox peaks of II-II', II-III' and IV-IV' are assigned to the reversible redox steps of molybdenum.[44,45] Figure 3B shows the cyclic voltammograms of the $Cs_2H_3PMo_{10}V_2O_{40}$-CPE at different scan rates (from 0.1 to 0.4 V•s^{-1}). There are four pairs of reversible redox peaks at $E_{1/2}$ of 0.505, 0.356, 0.197 and −0.048 V with the scan rate of 0.1 V•s^{-1}, where $E_{1/2}=(E_{pc}+E_{pa})/2$ and E_{pc} and E_{pa} denote the cathodic and anodic peak potentials, respectively. The peak potential values change gradually with the scan rate from 0.1 to 0.4 V•s^{-1}: the cathodic peak potentials shift toward the negative direction and the corresponding anodic peak potentials shift to the positive direction with increasing scan rate. Villabrille *et al.*[46] pointed that the reducibility of heteropolyanions could be determined by the highest redox potential value. Therefore, the first redox potential of $H_{3+n}PMo_{12-n}V_nO_{40}$ and $Cs_xH_{5-x}PMo_{10}V_2O_{40}$ in the present study was used to determine the redox ability of these catalysts. Figure 3C shows that the redox potential of $H_{3+n}PMo_{12-n}V_nO_{40}$ ($n=0$, 1, 2) increases with increasing the vanadium substitution number. According to the molecular orbital study on HPAs, the substitution of one or two addenda Mo^{6+} by less electronegative V^{5+} leads to the decrease of energy gap between the HOMO and the LUMO, accounting for the order of oxidizing power of $PMo_{12}O_{40}^{3-} < PMo_{11}VO_{40}^{4-} < PMo_{10}V_2O_{40}^{5-}$.[47] The effect of substitution of proton by Cs^+ on the redox ability of the catalysts was also investigated. As shown in Figure 3D, the redox potential decreases with increasing cesium content in $Cs_xH_{5-x}PMo_{10}V_2O_{40}$. Ai[48] also reported that the redox ability of $Cs_xH_{3-x}PMo_{12}O_{40}$ decreased with increasing replacement of proton by Cs^+.

2.2 Catalytic activity

The catalytic activity of pure heteropoly acids ($H_3PMo_{12}O_{40}$, $H_4PMo_{11}VO_{40}$ and $H_5PMo_{10}V_2O_{40}$) was tested in the hydroxylation of benzene reaction and the yield of phenol was 0.3%, 18.5% and 21.6%, respectively. However, these reactions in fact proceed in homogeneous system because of the high solubility of these heteropoly acids, thus the catalysts are difficult to be recycled. Considering the high activity of vanadium-substituted heteropoly acids, a series of cesium salts of heteropoly acids ($Cs_xH_{4-x}PMo_{11}VO_{40}$ and $Cs_xH_{5-x}PMo_{10}V_2O_{40}$) along with $CsH_2PMo_{12}O_{40}$ were prepared by solid synthesis method for heterogenization of the heteropoly acids. The catalytic

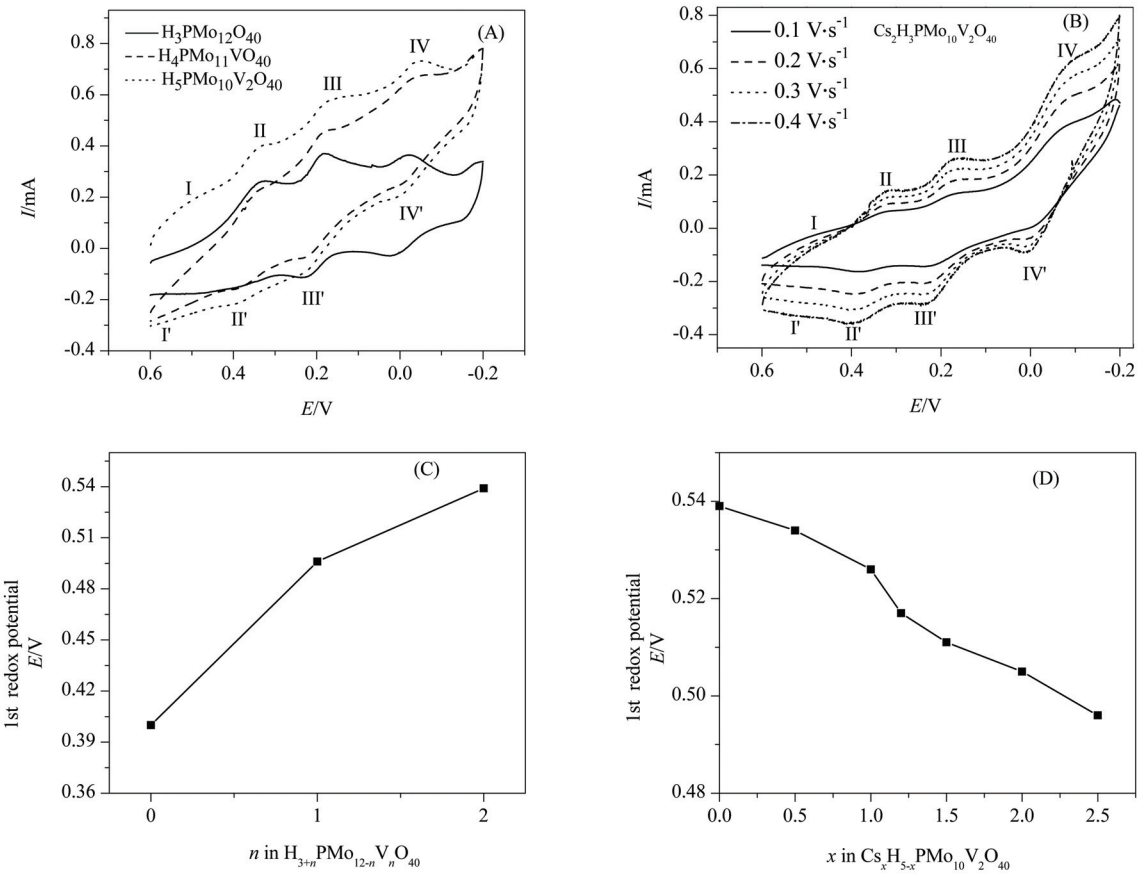

Figure 3 (A) The cyclic voltammograms of $H_{3+n}PMo_{12-n}V_nO_{40}$-CPE in an aqueous solution containing 0.5 mol•L^{-1} H_2SO_4 and 0.1 mol•L^{-1} Na_2SO_4 at the scan rate of 0.1 V•s^{-1}. (B) The cyclic voltammograms of $Cs_2H_3PMo_{10}V_2O_{40}$-CPE in an aqueous solution containing 0.5 mol/L H_2SO_4 and 0.1 mol•L^{-1} Na_2SO_4 at different scan rates. (C) Redox potential of $H_{3+n}PMo_{12-n}V_nO_{40}$ as a function of vanadium content. (D) Redox potential of $Cs_xH_{5-x}PMo_{10}V_2O_{40}$ as a function of cesium content

activity of these catalysts is shown in Figure 4. The yield of phenol was 17.2%, 18.0%, 15.9%, 12.4% and 10.3% over the $Cs_xH_{4-x}PMo_{11}VO_{40}$ catalysts with x values of 1, 1.5, 2, 2.5 and 3.0, respectively, and 18.5%, 18.7%, 20.2%, 20.4%, 19.2% and 15.1% over the $Cs_xH_{5-x}PMo_{10}V_2O_{40}$ catalysts with x values of 0.5, 1, 1.2, 1.5, 2 and 2.5, respectively. However, phenol yield was only 0.3% over $CsH_2PMo_{12}O_{40}$. The results show that the presence of vanadium species is essential for catalyzing the reaction and vanadium species is the active species. Furthermore, with the same cesium number the yield of phenol was higher over the $Cs_xH_{5-x}PMo_{10}V_2O_{40}$ catalysts than that over the $Cs_xH_{4-x}PMo_{11}VO_{40}$ catalysts, indicating that higher content of substituted vanadium atoms enhances the catalytic activity. The cyclic voltammetric results in Figure 3C show that $PMo_{10}V_2O_{40}^{5-}$ has higher redox ability than $PMo_{11}VO_{40}^{4-}$. Therefore, compared to the mono-vanadium substituted species the higher catalytic activity of the di-vanadium substituted species with the identical cesium number may be due to their higher redox ability.

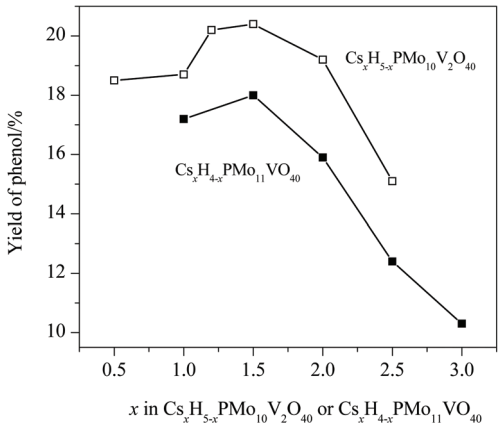

Figure 4 Catalytic activity of $Cs_xH_{4-x}PMo_{11}VO_{40}$ and $Cs_xH_{5-x}PMo_{10}V_2O_{40}$ for the benzene hydroxylation reaction
Reaction conditions: 30 mg catalyst, 0.5 mL (5.6 mmol) benzene, 5 mL 80.0% (φ) aqueous acetic acid solution as solvent, 1.2 mL 30% (w) H_2O_2 (11.6 mmol) as oxidant, 65 ℃, 3 h

Figure 4 shows the effect of cesium number of the catalysts on the catalytic activity. For a series of $Cs_xH_{5-x}PMo_{10}V_2O_{40}$ catalysts, phenol yield increased to 20.4% when the cesium number increased to 1.5, then decreased to 19.2% and 15.1% with further increase of the cesium number to 2 and 2.5, respectively. The similar trend in catalytic activity was also found over $Cs_xH_{4-x}PMo_{11}VO_{40}$ catalysts. The cyclic voltammetric behavior of $Cs_xH_{5-x}PMo_{10}V_2O_{40}$-CPE in Figure 3D shows that the redox ability of the catalysts decreases with increasing cesium number. Thus, the decrease of phenol yield with increasing cesium number could be explained by the decrease of the redox ability of the catalysts.[49,50] However, a contrary change of phenol yield under $x<1.5$ indicates that there is at least another factor arising from cesium number to affect the activity of the catalysts.

Okuhara *et al.*[22] reported that the hydrophobic nature of cesium salts of heteropoly acids would facilitate the accessibility of hydrophobic reactants to catalyst surface which make the catalysis proceed effectively. The ratio of the amount of adsorbed water to the adsorbed hydrocarbon can quantify the relative degree of hydrophobicity of catalyst.[51] To investigate the hydrophobic property of the $Cs_xH_{5-x}PMo_{10}V_2O_{40}$ catalysts, the amount of hydrophobic benzene and hydrophilic phenol adsorbed in the catalysts was analyzed. Figure 5 shows the dependence of benzene and phenol adsorption capacity on the cesium number of the $Cs_xH_{5-x}PMo_{10}V_2O_{40}$ catalysts. After reaching sorption equilibrium, the ratio of remaining phenol to benzene in the solution, n_{pH}/n_{BZ}, increases from 0.91 to 1.14 when the cesium number increases from 0 to 2.5, indicating that benzene adsorption capacity of the catalysts increases with increasing the cesium number. Therefore, the hydrophobicity of cesium salts of heteropoly acids increases with increasing cesium number, which may contribute to the improvement of the catalytic activity. Considering the synergistic effect between the redox ability and hydrophobicity of the catalysts with different cesium number, the catalytic activity increases to a maximum value and then decreases with increasing the cesium number of the catalysts.

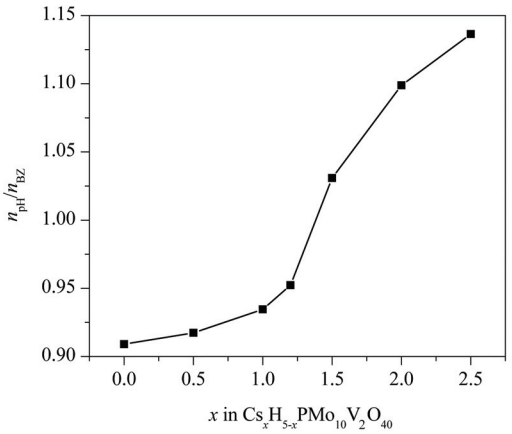

Figure 5 The dependence of benzene and phenol adsorption capacity on the Cs number of the $Cs_xH_{5-x}PMo_{10}V_2O_{40}$ catalysts (the value of n_{PH}/n_{BZ} is the molar ratio of remaining phenol and benzene in the solution after reaching sorption equilibrium)

From a practical point of view, the leaching of the catalyst into solution should be minimized. In the present case, the released heteropolyanions in the solution were detected with UV-Vis spectroscopy. The absorption band of $PMo_{10}V_2O_{40}^{5-}$ in the solution centered at 306 nm (the insert of Figure 6A) is attributed to the charge transfer of the oxygen ligand to octahedral coordinated metal,[52] which was selected to measure the content of catalysts in solution. In the leaching test, a comparative experiment showed that the release of the catalyst in the acetic acid solvent was nearly the same as that under reaction conditions, indicating the insignificant effect of H_2O_2 on the leaching of the catalyst. The effect of cesium number on the leaching of the heteropoly species is shown in Figure 6A. For the $Cs_xH_{4-x}PMo_{11}VO_{40}$ catalysts, the amount of released heteropolyanions decreases rapidly from 41.6% to 1.8% when x increases from 1 to 3. For the $Cs_xH_{5-x}PMo_{10}V_2O_{40}$ catalysts, the amount of released heteropolyanions also decreases rapidly from 66.1% to 5.0% and 1.4% when x increases from 0.5 to 2 and 2.5, respectively, which indi-

cates that increasing cesium number favors the insolubility of the catalysts.

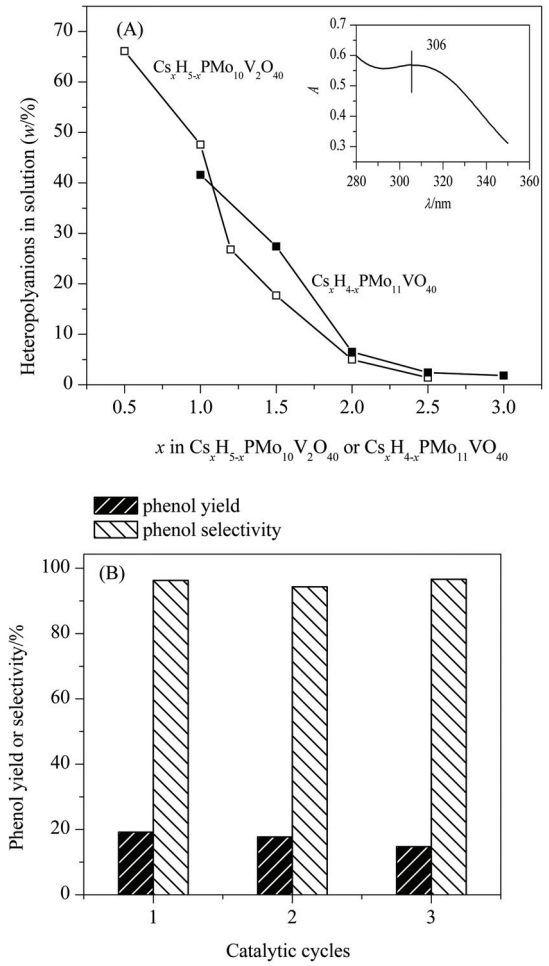

Figure 6 (A) The amount of heteropoly species released from $Cs_xH_{4-x}PMo_{11}VO_{40}$ and $Cs_xH_{5-x}PMo_{10}V_2O_{40}$ as a function of Cs number and the UV-Vis spectrum of $PMo_{10}V_2O_{40}^{5-}$ (insert) and (B) the catalytic recycle of the $Cs_2H_3PMo_{10}V_2O_{40}$ catalyst

Among the $Cs_xH_{3+n-x}PMo_{12-n}V_nO_{40}$ samples (n=0, 1, 2, x=0.5—3.0), $Cs_2H_3PMo_{10}V_2O_{40}$ shows high phenol yield (19.2%) and turnover number of 71.7 (TON=molar number of phenol/molar number of catalyst) with limited leaching during the catalytic reaction. The H_2O_2 efficiency over $Cs_2H_3PMo_{10}V_2O_{40}$ is 10.9%, which is comparable with other vanadium-based catalysts[53]. In addition, after the filtration of $Cs_2H_3PMo_{10}V_2O_{40}$ no significant benzene conversion was found in the filtrate and the used catalyst exhibited high catalytic activity during the third run (shown in Figure 6B), indicating the heterogeneous catalysis of $Cs_2H_3PMo_{10}V_2O_{40}$. Furthermore, IR spectrum and XRD pattern of the used $Cs_2H_3PMo_{10}V_2O_{40}$ catalyst are almost the same as those for the fresh one (shown in Figure 1 and Figure 2), suggesting that the Keggin structure of the catalyst has no change during the reaction. Furthermore, a comparison of reaction activity on various typical catalysts for the hydroxylation of benzene to phenol with H_2O_2 as oxidant is presented in Table 1, where $Cs_2H_3PMo_{10}V_2O_{40}$ shows remarkable catalytic performance.

Table 1 The catalytic performance of various catalysts on hydroxylation of benzene to phenol

Catalyst	Temp./℃	Yield (Y) and Selectivity (S)	Reference
$[(CH_3)_4N]_4PMo_{11}VO_{40}$	60	Y=12.4, S=85.7	[54]
$H_5PMo_{10}V_2O_{40}/NH_2$-SBA-15	60	Y=19.0, S=95.0	[55]
Fe_3O_4/MWCNTs	60	Y=14.4, S=92.7	[56]
VO_x/SBA-16	60	Y=13.8, S=97.5	[57]
V_2O_5/Al_2O_3	65	Y=9.3, S=93.0	[58]
$Cs_2H_3PMo_{10}V_2O_{40}$	65	Y=19.2, S=96.3	This work

3 Conclusions

$Cs_xH_{3+n-x}PMo_{12-n}V_nO_{40}$ catalysts (n=0, 1, 2, x=0.5—3.0) were synthesized by the solid synthesis method and tested in the direct hydroxylation of benzene reaction. The redox ability of the catalysts decreases gradually and the hydrophobicity of the catalysts increases with increasing Cs^+ substitution number. The catalytic activity of the catalysts is dependent on the vanadium substitution number and cesium content which may arise from the combined effects of the redox ability and hydrophobicity of the catalysts. Also the amount of released heteropoly species into the solution decreases significantly with increasing the cesium content. Among the catalysts studied, $Cs_2H_3PMo_{10}V_2O_{40}$ exhibits high phenol yield (19.2%) and only limited leaching. The cesium salts of vanadium substituted Keggin-type heteropoly acids can be used as highly effective heterogeneous catalysts for the direct hydroxylation of benzene.

4 Experimental

The purchased chemicals (analytical grade) were used without further purification. Heteropoly acids were prepared with the conventional methods.[35,36] In the synthesis of $H_5PMo_{10}V_2O_{40}$, 3.1 g of $NaVO_3$•$2H_2O$ was dissolved in 50 mL of boiling water and then mixed with 3.55 g of Na_2HPO_4•$12H_2O$ dissolved in 50 mL of water. After the solution was cooled down to room temperature, 2.5 mL of concentrated sulfuric acid was added, followed with 24.0 g of Na_2MoO_4•$2H_2O$ dissolved in 100 mL of water. 42.5 mL of concentrated sulfuric acid was further added slowly with vigorous stirring, and the color changed from dark red to light red. The heteropoly acid was extracted with 250 mL of diethyl ether at the middle layer as a heteropoly etherate. The ether was removed by evaporating at room temperature for 12 h. The solid obtained was dissolved in water and concentrated until the red crystals appeared. Then the crystals were dried in an oven at 50 ℃ for 12 h. Other two heteropoly acids, $H_3PMo_{12}O_{40}$ and $H_4PMo_{11}VO_{40}$, were prepared with the similar process.[35,36]

Cesium salts of HPAs with different cesium contents were prepared by the solid synthesis method. The typical procedure for preparation of $CsH_4PMo_{10}V_2O_{40}$ was described as follows. Equal mole of $CsNO_3$ and $H_5PMo_{10}V_2O_{40}$•$9H_2O$ were ground in a ball mill for 0.5 h at room temperature. Then the obtained solid powder was dried in an oven at 120 ℃ overnight. $Cs_xH_{4-x}PMo_{11}VO_{40}$

(x=1—3) and $Cs_xH_{5-x}PMo_{10}V_2O_{40}$ (x=0.5—2.5) were prepared by the same method.

XRD patterns were recorded on a Bruker D8 Advanced X-ray diffractometer using Cu Kα radiation with a voltage of 40 kV and a current of 60 mA. IR spectra were recorded on a NEXUS 470 FT-IR spectrometer using powder mixture of catalysts and KBr. Elemental analysis was performed on a Thermo Elemental IRIS Intrepid ICP-AES spectrometer.

$Cs_xH_{3+n-x}PMo_{12-n}V_nO_{40}$ (n=0, 1, 2, x=0.5—3.0) modified carbon paste electrodes were prepared as follows. Graphite powder (0.5 g) and $Cs_xH_{3+n-x}PMo_{12-n}V_nO_{40}$ sample (20 mg) were mixed and ground by an agate mortar, then paraffin oil (0.06 mL) was mixed. The homogenized mixture was packed into a glass tube with inner diameter of 3 mm and one end of the tube surface was polished. Electrical contact was established with a copper rod through the other end of the electrode. The cyclic voltammograms were obtained with a CHI 821 electrochemical workstation at room temperature. The platinum gauze and Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. $Cs_xH_{3+n-x}PMo_{12-n}V_nO_{40}$ modified carbon paste electrode was used as a working electrode and an aqueous solution containing 0.5 mol•L^{-1} H_2SO_4 and 0.1 mol•L^{-1} Na_2SO_4 was used as the electrolyte solution.

In order to study the benzene and phenol adsorption capacity of the catalysts, 30 mg of catalyst was added into 5 mL of aqueous acetic acid solution containing equal mole (11.3 μmol) of benzene and phenol with stirring for 2 h at room temperature to achieve sorption equilibrium. Then, the molar numbers of the remaining benzene (n_{BZ}) and phenol (n_{PH}) in the solution were measured by gas chromatography. The ratio of n_{pH}/n_{BZ} indicates the relative phenol and benzene adsorption capacity of the catalysts, *e.g.* a n_{pH}/n_{BZ} value of more than 1 indicates a catalyst exhibits higher adsorption capacity of benzene than that of phenol.

The leaching of heteropoly species was studied by measuring the concentration of heteropolyanions in the aqueous acetic acid solution based on the absorbance around 306 nm after stirring at 65 ℃ for 3 h using Shimadzu UV-2450 spectrometer. The identical concentration of acetic acid solution was used as the reference.

Direct hydroxylation of benzene to phenol with H_2O_2 as oxidant was carried out in a three-necked 25 mL round bottom flask connected with a reflux condenser. A typical reaction was carried out as follows. 30 mg of the catalyst, 0.5 mL (5.6 mmol) of benzene and 5 mL of 80.0% (φ) aqueous acetic acid solvent were added into the flask. After heating the mixture to 65 ℃ under stirring, 1.2 mL (11.6 mmol) of 30% (w) hydrogen peroxide was added dropwise in *ca.* 30 min. After 3 h of reaction, the catalyst was separated by centrifugation. The content of liquid products was analyzed by a gas chromatography equipped with a HP-5 capillary column and a FID. The products were confirmed by comparing with the retention time of the standard samples and also by GC/MS. Toluene was used as an internal standard to quantify the amount of phenol formed.

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(Zhao, X.)

