Direct hydroxylation of benzene to phenol with hydrogen peroxide catalyzed by a quinine heteropolyacid hybrid

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Article (Dedicated to Professor Yi Chen on the occasion of his 80th birthday)

Direct hydroxylation of benzene to phenol with hydrogen peroxide catalyzed by a quinine-heteropolyacid hybrid

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ABSTRACT

A new heterogeneous hybrid catalyst designed for direct hydroxylation of benzene to phenol was prepared through modification of Keggin-structured phosphovanadomolybdate with quinine. The structure of the catalyst was fully characterized by Fourier transform infrared and ultraviolet-visible spectroscopies, X-ray diffraction, scanning electron microscopy, thermogravimetric analysis, nitrogen sorption experiments, and CHN elemental analysis. The results indicated that the hybrid catalyst was a semi-amorphous heteropolyacid salt with high thermal stability, surface area, and pore volume. The catalytic activity of the hybrid for the hydroxylation of benzene with H_2O_2 was assessed. The hybrid catalyst forms a liquid-solid biphasic system and exhibits high activity, convenient recovery, and reusability. The strong electronic interactions and hydrogen bonding networks formed between the π-electron-rich quinine framework and heteropolyanions are responsible for the solid nature and insolubility of the catalyst. The high surface area and improved redox properties of the Keggin heteropolyacid account for its excellent catalytic performance. The results of this work reveal a new, more facile way to prepare an efficient polyoxometalate-based catalyst for heterogeneous hydroxylation of benzene to phenol.

1. Introduction

The three-step cumene process first reported by Hock and Lang [1] in 1944 is still widely used industrially to produce phenol even though it suffers from disadvantages including low atom utilization, high energy consumption, and environmental pollution [2]. Direct hydroxylation of benzene using clean oxidants like N_2O [3], O_2 [4], H_2O_2 [5], as well as the H_2-O_2 system with Pd-based composite membrane reactors [6,7] has attracted great attention even though it is one of the most difficult oxidation reactions in organic synthesis [6]. For H_2O_2-based hydroxylation of benzene, Schiff bases [8], molecular sieves including TS-1 and V-MCM-41 [9,10], and polyoxo-metalates (POMs) [11] have been used as catalysts. Among them, V-containing POM catalysts have shown high yields for phenol [12,13]. However, it is very difficult to isolate these catalysts because POMs readily dissolve in the reaction system. To prevent this issue, heterogenization of POMs is an interesting possibility to improve their potential for direct hydroxylation of benzene.

Immobilization of POMs on porous supports is commonly used to heterogenize POM catalysts. However, this approach always suffers from a slow reaction rate and/or leaching of active sites [14]. Recently, modification of POMs with organic units such as ionic liquids (ILs), organometallic complexes, and organic polymers has been used to prepare POM-based organ-

ic-inorganic hybrid heterogeneous catalysts [15–17]. We previously prepared a series of POM-based hybrid catalysts for use in many acid-catalyzed and oxidation organic syntheses [18–21]. Direct hydroxylation of benzene using functionalized IL- or cross-linked ionic copolymer-modified POM-based heterogeneous catalysts has been studied [22,23]. Although high activity and convenient recoverability were realized, complex steps and a large amount of organic solvent were required to prepare these catalysts. Pyridine-POM salts have also been employed as effective catalysts for direct hydroxylation of benzene [24]. The excellent performance of POM salts arises because the redox properties of the POM are improved by the stretch of conjugated π-electrons in the pyridine ring. However, pyridine-POM is a homogeneous catalyst for hydroxylation of benzene, which makes it difficult to isolate and reuse. Therefore, an environmentally friendly, simple to prepare, inexpensive, and highly efficient heterogeneous POM-based catalyst for direct hydroxylation of benzene remains a challenge.

In this work, we prepare a quinine-phosphovanadomolybdate ($H_5PMo_{10}V_2O_{40}$, V_2) (Q-V_2) solid-state hybrid catalyst by attaching a cinchona alkaloid structure composed of three basic molecular units: a quinoline ring, a quinuclidine ring (tertiary amine), and a methylenic alcohol group linking the two to Keggin-structured V_2 using environmentally friendly H_2O and ethanol as solvents (Scheme 1). We use this hybrid catalyst for direct hydroxylation of benzene to phenol with H_2O_2 as the oxidant. Although cinchona alkaloids are widely used in organic synthesis, they have not been investigated for direct hydroxylation of benzene. The Q-V_2 catalyst leads to the desirable liquid-solid heterogeneous hydroxylation of benzene systems, exhibiting high activity and good recyclability. In addition, the Q-V_2 catalyst possesses the advantages of being inexpensive, environmentally friendly, and convenient to prepare.

2. Experimental

2.1. Catalyst preparation

All chemicals were of analytical grade from Shanghai Chem.

Reagent Co. and used as received. Keggin-structured V-containing heteropolyacid (HPA) V_2 was prepared according to a procedure described previously [24]. MoO_3 (16.59 g, 0.115 mol) and V_2O_5 (2.10 g, 0.0115 mol) were mixed with deionized water (250 mL) in a flask reactor equipped with a water-cooled condenser and magnetic stirrer, and then heated to 120 °C under vigorous stirring. Concentrated H_3PO_4 (85%, 1.33 g, 0.0115 mol) was dissolved in water (10 mL) and then added dropwise to the above mixture within 30 min. After stirring for 24 h at 120 °C, an orange-red solution formed. As the solution was cooled to room temperature, orange fine powder was got by a vacuum drying at 50 °C for 24 h. The final product $PMoV_2$ was obtained by re-crystalizing the powdered solid in deionized water and another vacuum drying at 50 °C for 24 h.

The Q-V_2 solid-state hybrid was prepared through the reaction of quinine and V_2 with a molar ratio of 2.5:1 in water. The obtained orange precipitate was filtered, washed with distilled water (4×100 mL), and then dried under vacuum at 80 °C for 24 h to give Q-V_2 as a powder (yield: 92%). Its BET specific surface area was 27 m²/g. Elemental analysis (%) Calcd: C, 23.59; N, 2.75; H, 2.36. Found: C, 23.95; N, 2.83; H, 2.78.

Control materials, $[TMA]_5$-V_2, Py_5-V_2, and $[quinoline]_5$-V_2, the chemical structure of which is presented in Scheme 2, were prepared similarly by reacting the respective organic precursor with V_2 in a molar ratio of 5:1. The classical heterogeneous supported catalyst $PMoV_2/SiO_2$ was prepared by impregnating porous silica gel with V_2. The measured BET specific surface area of $PMoV_2/SiO_2$ was 242 m²/g with an estimated vanadium loading of 0.23 mmol/g from inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis.

2.2. Catalyst characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 360 FT-IR spectrometer (KBr discs) in the region of 4000–400 cm⁻¹. Elemental analyses were performed on a CHN elemental analyzer (FlashyEA 1112). The vanadium loading in the supported catalyst was determined by ICP-AES (Jarrell-Ash 1100). Electron spin resonance (ESR) spectra were
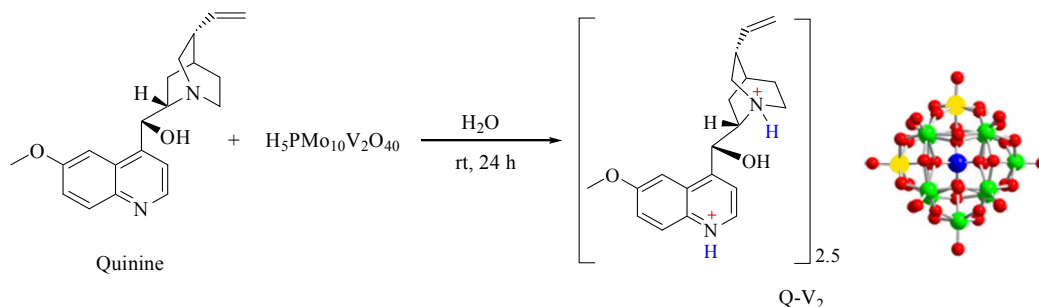
Scheme 1. Synthesis of quinine-doped heteropolyacid salt Q-V_2.
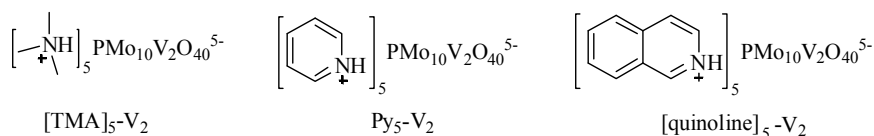
Scheme 2. Control organic-doped HPA salt catalysts.

recorded on a Bruker EMX-10/12 spectrometer at X-band. Measurements were performed at –110 °C in a frozen solution using a liquid/gas nitrogen temperature regulation system controlled by a thermocouple located at the bottom of the microwave cavity within a Dewar insert. Solid ultraviolet-visible (UV-Vis) spectra were obtained with a PE Lambda 950 spectrometer, and BaSO$_4$ was used as an internal standard. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance powder diffractometer using a Ni-filtered Cu K_α radiation source from 5° to 50° with a scan rate of 2°/min at 40 kV and 20 mA. The samples were pre-dried at 100 °C for 2 h before measurement. BET surface areas were measured at the temperature of liquid nitrogen using a Micromeritics ASAP 2010 analyzer. The samples were degassed at 150 °C to a vacuum of 10^{-3} Torr before analysis. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 field-emission scanning electron microscope. Thermogravimetric (TG) analysis was carried out with a Netzsch STAY 409 instrument in dry air at a heating rate of 10 °C/min.

2.3. Catalytic test

Benzene (0.78 g, 10 mmol), a mixture of acetonitrile and acetic acid (volume ratio 1:1, 6 mL), and catalyst (0.1 g) were added to a 25 mL flask reactor. Then, aqueous H$_2$O$_2$ (30%, 30 mmol) was added dropwise to the stirred mixture in the reactor within 30 min. The reaction time began after the addition of H$_2$O$_2$. Typical reaction temperature and time were 70 °C and 4 h, respectively. After reaction, the mixture was centrifuged to remove the solid catalyst, and then the liquid was analyzed by a gas chromatograph (GC; SP-6890A) equipped with a flame ionization detector and capillary column (SE-54 30 m × 0.32 mm × 0.3 μm). The temperature of the GC column oven was held at 70 °C for 5 min and then increased to 140 °C at a rate of 6 °C/min. Under these conditions, only phenol was detected as a product. No GC signals from catechol, hydroquinone, or benzoquinone were observed, i.e., the selectivity for phenol was 100%. 1,4-Dioxane was used as an internal standard to calculate the yield of phenol (yield of phenol (based on benzene) = mmol phenol/mmol initial benzene).

To test the catalytic recyclability of Q-V$_2$, after reaction, the catalyst was separated by filtration, washed with acetic acid (3 × 20 mL) and then dried under vacuum at 80 °C for 6 h. The recovered catalyst was reused in the next run.

3. Results and discussion

3.1. Catalytic performance of Q-V$_2$ for hydroxylation of benzene

Table 1 compares the performance of the various catalysts for hydroxylation of benzene with H$_2$O$_2$. No phenol was detected in the absence of catalyst (entry 1) or by using quinine or V-free H$_3$PMo$_{12}$O$_{40}$ as the catalyst (entries 2 and 3). When pure V$_2$ was used as the catalyst, a yield of phenol of 24.5% with selective conversion of H$_2$O$_2$ of 8.2% was achieved (entry 4), which is consistent with previous reports that show the V ions in HPA anions are catalytically active centers for hydrox-
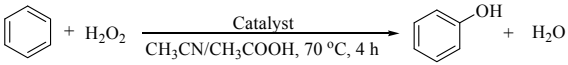
ylation of benzene to phenol [12,13]. However, pure V$_2$ is a homogeneous catalyst that is difficult to isolate and reuse. In contrast, the quinine-doped catalyst Q-V$_2$ remained insoluble throughout the hydroxylation reaction, thus forming a liquid-solid heterogeneous catalysis system. Using Q-V$_2$, the yield of phenol was 23.6%, and the selective conversion of H$_2$O$_2$ was 7.9% (entry 5). Such catalytic performance is comparable to that of homogeneous V$_2$, suggesting that heterogenization does not cause a significant decrease in the activity of V species.

For comparision, the conventional heterogeneous catalyst PMoV$_2$/SiO$_2$ was prepared by supporting V$_2$ on porous silica via impregnation. Low catalytic activity was observed for this catalyst: the phenol yield was 13.8% and the selective conversion of H$_2$O$_2$ was 4.6% (entry 6), consistent with previous results [22–26]. The above observations indicate that the quinine-doped organic HPA salt Q-V$_2$ not only generates a heterogeneous catalytic system but also maintains similar activity to its homogeneous analog. In addition, Q-V$_2$ is much more active and efficient than the conventional heterogeneous catalyst obtained by impregnation.

To clearly illustrate the role of quinine, three control samples, [TMA]$_5$-V$_2$, Py$_5$-V$_2$, and [quinoline]$_5$-V$_2$, were prepared using different organic modifiers. For example, a 24.3% yield of phenol and selective conversion of H$_2$O$_2$ of 8.1% were obtained using the known organic HPA salt of the quaternary amine cation [TMA]$_5$-V$_2$ (entry 7). Notably, [TMA]$_5$-V$_2$ was insoluble during the early stage of the reaction but it dissolved gradually upon the addition of H$_2$O$_2$, resulting in a homogeneous reaction. Pyridine-doped catalyst Py$_5$-V$_2$ (entry 8) prepared by directly mixing Py with V$_2$ also induced a homogeneous reaction but gave a lower yield and selective conversion of H$_2$O$_2$ than [TMA]$_5$-V$_2$. Control catalyst [quinoline]$_5$-V$_2$ (entry 9) contained similar quinine structure to Q-V$_2$, but it still formed a homogeneous reaction system, giving a phenol conversion of 22.4% and selective conversion of H$_2$O$_2$ of 7.5%. These results indicate that it is not easy to prepare insoluble, doped organic HPA salt catalysts for the heterogeneous hydroxylation of benzene with H$_2$O$_2$. This is mainly because Keggin-structured HPA catalysts

Table 1

Performance of various catalysts for the hydroxylation of benzene with H$_2$O$_2$.

Entry	Catalyst	Reaction type	Y [a]/%	X(H$_2$O$_2$) [b]/%
1	none	homogeneous	0	0
2	quinine	homogeneous	0	0
3	H$_3$PMo$_{12}$O$_{40}$	homogeneous	0	0
4	V$_2$	homogeneous	24.5	8.2
5	Q-V$_2$	heterogeneous	23.6	7.9
6	PMoV$_2$/SiO$_2$	heterogeneous	13.8	4.6
7	[TMA]$_5$-V$_2$	homogeneous	24.3	8.1
8	Py$_5$-V$_2$	homogeneous	21.2	7.1
9	[quinoline]$_5$-V$_2$	homogeneous	22.4	7.5

Reaction conditions: catalyst (0.04 mmol for entries 1–5 and 7–9; 0.35 g for entry 6), benzene (10 mmol), mixture of acetonitrile and acetic acid (6 mL, volume ratio of 1:1), 30% H$_2$O$_2$ (30 mmol), 70 °C, 4 h.
[a] Yield of phenol = n(phenol)/n_0(benzene).
[b] Selective conversion of H$_2$O$_2$ = n(phenol)/n_0(H$_2$O$_2$).

tend to be labile, degradable, and/or soluble in the presence of H_2O_2 [27]. Therefore, during the heterogenization process, quinine plays the important role of keeping the catalyst insoluble in the reaction system.
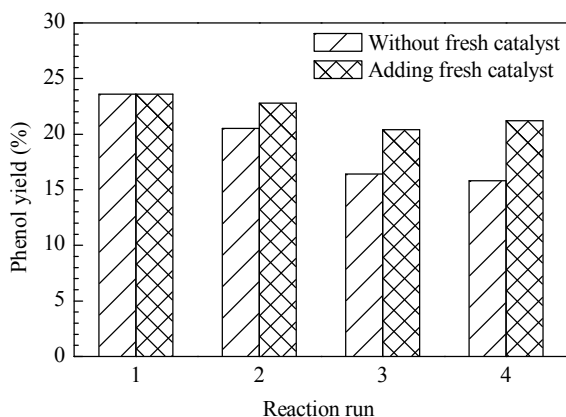
3.2. Catalyst reusability

The reusability of a heterogeneous catalyst is important, so we measured the catalytic recyclability of Q-V_2 using a four-run test, as shown in Fig. 1. In each cycle, the catalyst Q-V_2 was recovered by filtration from the reaction mixture, dried, and then directly used in the next cycle without further treatment. The recovery ratio of the catalyst was greater than 90%. If no fresh catalyst was added to the recovered catalyst, the yield of phenol decreased slowly as the catalyst was reused numerous times (Fig. 1), with yields of 20.5%, 16.4%, and 15.8% for the second, third, and fourth runs, respectively. The slow decrease of yield is attributed to the loss of some catalytic active sites during reaction and recovery rather than to a decrease of activity caused by the formation of coke in the reaction or distortion of the catalyst structure.

When a small amount of fresh catalyst was added to the recovered one to keep the amount of catalyst in each run constant, the yield of phenol was 22.8%, 20.4%, and 21.2% for the second, third, and fourth runs, respectively. Although the catalytic activity still reduced slightly for each cycle, the deactivation rate of the catalyst was considerably slower than when no fresh catalyst was added (Fig. 1). This phenomenon indicates that the heterogeneous catalyst Q-V_2 can be reused effectively after simple filtration. Meanwhile, this again proposes that the decrease of activity of the recovered catalyst is caused by the leaching of catalytic active centers, unlike conventional supported catalysts, which are deactivated mostly because of coke formation [28].

3.3. Understanding catalytic performance

Elemental analysis of Q-V_2 indicated that it forms with an initial molar ratio of quinine to V_2 of 2.5:1. Elemental analysis of the recovered catalyst after four runs gave similar values to
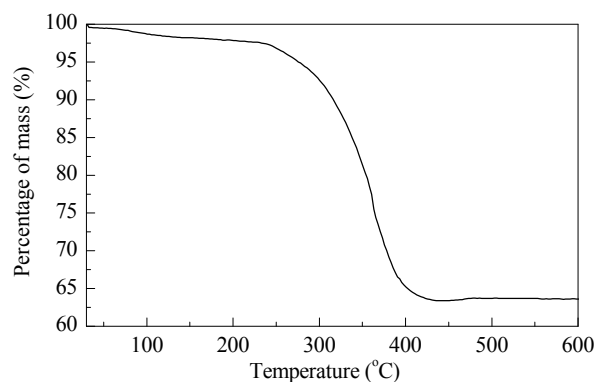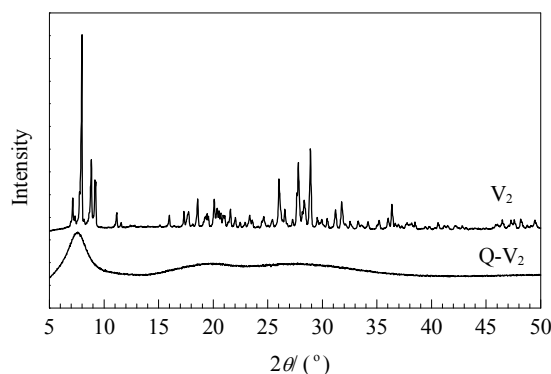

Fig. 2. TG curve measured for Q-V_2.

those determined for the fresh catalyst. This suggests that coking does not occur during the catalytic reaction. Figure 2 displays a TG curve measured for Q-V_2. The slight mass loss below 230 °C is assigned to the desorption of adsorbed water, suggesting high thermal stability of up to 230 °C. The drastic mass loss observed above 230 °C is attributed to the complete decomposition of the organic moiety, as well as the subsequent collapse of the inorganic HPA structure. The total mass loss is 34% in the range of 230–430 °C, consistent with the theoretical prediction of 33.5%. These results further confirm that the structure of Q-V_2 shown in Scheme 1 is correct.

XRD patterns of V_2 and Q-V_2 are depicted in Fig. 3. Pure V_2 presents a set of diffraction peaks consistent with the secondary structure of an inorganic HPA crystal [22]. However, for the hybrid catalyst Q-V_2, these characteristic peaks disappear, and only a weak, broad diffraction of around 7.8° is observed, which implies that during the synthesis of Q-V_2, the crystal structure of the HPA precursor is rearranged by introducing the large organic cation quinine, affecting the self-assembly of cations and anions through electrostatic interactions, hydrogen bonds, and Van der Waals forces [29].

Figure 4 shows a nitrogen sorption isotherm measured for Q-V_2, which is type IV with a small hysteresis loop in the p/p_0 from 0.08 to 1.0, suggesting typical mesostructure with relative large pore size (the average pore size is 39 nm, Table 2). Based on the desorption branch of the isotherm, Q-V_2 has a high BET surface area of 27 m^2/g and large pore volume of 0.27 cm^3/g, which are much higher than those of pure V_2 with a surface area of 10 m^2/g and pore volume of 0.036 cm^3/g (Table 2).

Fig. 1. Reusability of Q-V_2 catalyst for the hydroxylation of benzene with H_2O_2. Reaction conditions: molar ratio of H_2O_2 to benzene = 3:1, mixture of acetonitrile and acetic acid (volume ratio 1:1, 6 mL), 70 °C, 4 h.

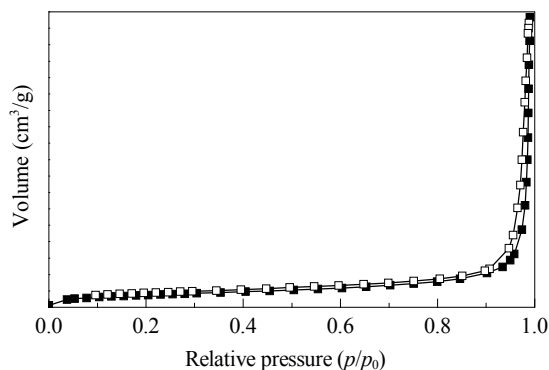**Fig. 3.** XRD patterns measured for V_2 and Q-V_2.

Fig. 4. Nitrogen adsorption-desorption isotherm measured for Q-V₂.

Table 2
Nitrogen sorption results of catalysts.

Catalyst	A_{BET} (m²/g)	Pore volume (cm³/g)	Average pore diameter (nm)
V₂	10	0.036	15
Q-V₂	27	0.27	39

Fig. 6. FT-IR spectra of V₂ (1), quinine (2), Q-V₂ (3), and recycled Q-V₂ after four runs (4).

Figure 5 shows the SEM images of Q-V₂ before and after four runs. The fresh catalyst possesses sponge-like morphology, and the small particles interact with each other to form mesopores, consistent with the nitrogen sorption results. In contrast, the recovered catalyst partly changes to a layered structure (Fig. 5(b)), which may be responsible for the decrease in activity of the recovered catalyst.

Generally, the activity of a heterogeneous catalyst is limited by mass transfer during the diffusion process. The heterogeneous Q-V₂ catalyst exhibits the similar performance to its homogeneous analog. The cavities between cations and anions may allow the substrates and oxidant H_2O_2 to permeate into the bulk of the catalyst structure [29], through which the well-known catalytic intermediate V^{5+} peroxo species in the bulk of the catalyst could act as the active centers for hydroxylation of benzene, i.e., the heterogeneous reaction takes place via typical bulk-type catalysis. In addition, the increased surface area and presence of mesopores in Q-V₂ allow easy diffusion and access of the substrate and oxidant H_2O_2 molecules to the HPA framework [30] and promote pseudoliquid behavior. Therefore, heterogeneous Q-V₂ can retain high catalytic activity even after four cycles of use.

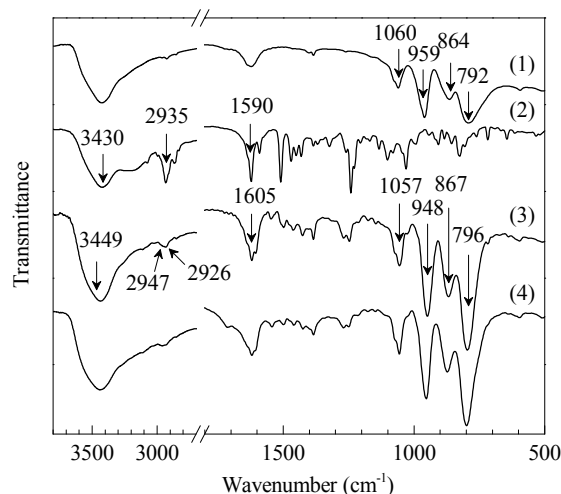FT-IR spectra of the catalysts are illustrated in Fig. 6. Four characteristic bands are observed at 1060, 959, 864, and 792 cm⁻¹ for pure V₂ (Fig. 6(1)) with Keggin structure, which are assigned to the asymmetric stretching vibrations of the central oxygen bond (P–O) for PO_4 tetrahedra, terminal oxygen (M=O), and inter- and intra-octahedral oxygen (M–O$_b$–M and M–O$_c$–M), respectively [31]. For the hybrid catalyst Q-V₂ (Fig. 6(3)), the four bands characteristic of HPA ions with Keggin structure can be still detected, suggesting that the Keggin framework remains even after the protons of HPA are substituted by organic cations. However, these peaks shift slightly, implying slight distortion of the Keggin HPA framework caused by the extension of the conjugated electrons of organic cations to HPA anions [32]. Meanwhile, the FT-IR spectrum of quinine shows the C=N stretch of the quinoline ring at 1590 cm⁻¹ (Fig. 6(2)). This peak shifts to 1605 cm⁻¹ for Q-V₂ because of protonation [33]. The FT-IR results suggest that Q-V₂ is composed of ionically linked protonated quinine cations and Keggin-structured HPA anions.

The broad bands observed at 3430 and 2935 cm⁻¹ for quinoline (Fig. 6(2)) assigned to H–O vibrations and aliphatic C–H stretching vibration, respectively, shift to 3449 cm⁻¹ and split clearly into two bands at 2947 and 2926 cm⁻¹ for Q-V₂. These results indicate the formation of extended hydrogen-bonding networks between HPA anions and organic cations [34]. These hydrogen-bonding networks, as well as the large volume and high valence of HPA anions, may account for the solid nature of
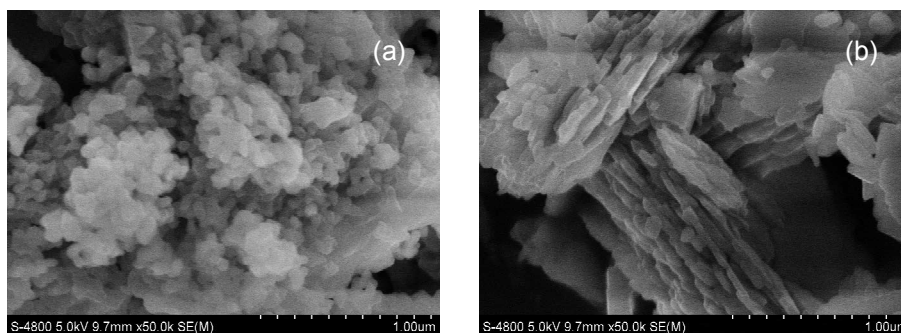

Fig. 5. SEM images of fresh catalyst Q-V₂ (a) and recycled Q-V₂ after four runs (b).
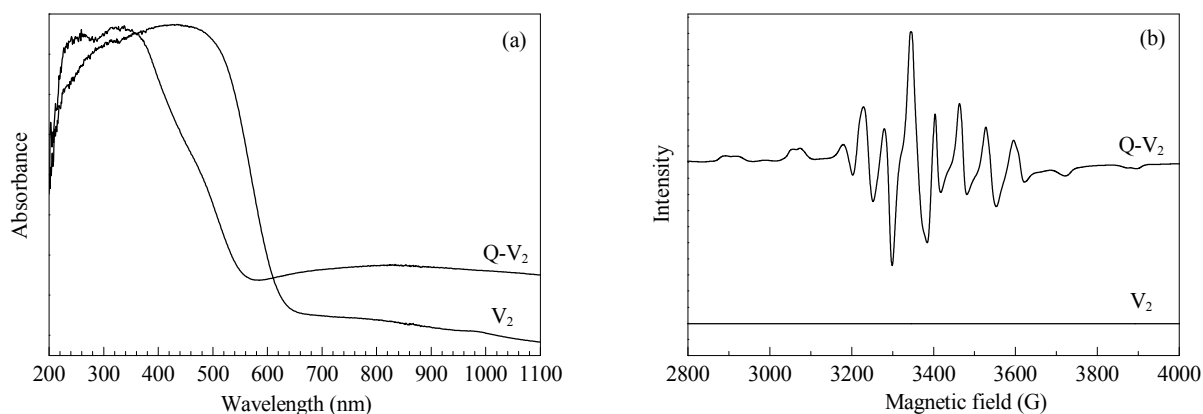
Fig. 7. UV-Vis spectra (a) and ESR spectra (b) of V_2 and Q-V_2.

the hybrid catalyst Q-V_2. Meanwhile, the hydroxyl groups in the quinine structure favor the adsorption of H_2O_2 during the catalytic reaction, resulting in a considerable increase of catalytic activity, which is in good agreement with results published previously showing that the hydrophilicity/hydrophobicity of a catalyst will affect its activity [35]. The recovered Q-V_2 catalyst (Fig. 6(4)) exhibits similar bands to the fresh one, indicating that the chemical structure of the catalyst is not changed during the catalytic reaction.

Figure 7(a) compares the UV-Vis spectra for V_2 and Q-V_2. The broad absorption band at 400 nm for V_2 is assigned to the charge transfer reaction of $O^{2-} \rightarrow V^{5+}$ in Keggin HPA anions [36]. In contrast, the $O^{2-} \rightarrow V^{5+}$ band for Q-V_2 shifts to 340 nm, accompanied with a large broad band from 600 to 1000 nm for $V^{5+} \rightarrow V^{4+}$. The reduced V^{4+} species is formed by the electron interaction between the organic cations and HPA anions [37]. Figure 7(b) shows the ESR spectra for V_2 and Q-V_2. V_2 did not exhibit a response, whereas an eight-line signal consistent with V^{4+} species was observed for Q-V_2. Therefore, both UV-Vis and ESR results reveal the presence of V^{4+} species in Q-V_2, indicating the strong electronic interaction between Keggin units and quinine. It is thus proposed that the high activity of Q-V_2 for the hydroxylation of benzene is associated with not only the increased surface area and promotion of quinine hydroxyl groups but also with the redox properties of the HPA anions being improved by the electronic interaction between Keggin units and quinine. Accordingly, the lower yield obtained over the silica-supported catalyst PMoV$_2$/SiO$_2$ (Table 1, entry 9), even though it has high BET surface area, is because PMoV$_2$/SiO$_2$ lacks the strong interaction between Keggin units and quinine.

4. Conclusions

A new hybrid catalyst quinine-phosphovanadomolybdate (Q-V_2) for hydroxylation of benzene to phenol with aqueous hydrogen peroxide was easily prepared by reacting quinine with a Keggin HPA. The catalyst formed a solid-liquid heterogeneous catalytic system and exhibited high catalytic performance, with comparable activity to its homogeneous analog, easy recoverability, and good reusability. The highly efficient performance of Q-V_2 was a result of its high surface area, pore volume, and promotion by quinine hydroxyl groups, as well as the redox properties of the Keggin HPA anion being improved by the strong electronic interaction between the π-electron-enriched quinine framework and HPA anions.

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Graphical Abstract

Direct hydroxylation of benzene to phenol with hydrogen peroxide catalyzed by a quinine-heteropolyacid hybrid

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Phenol yield: 23.6%
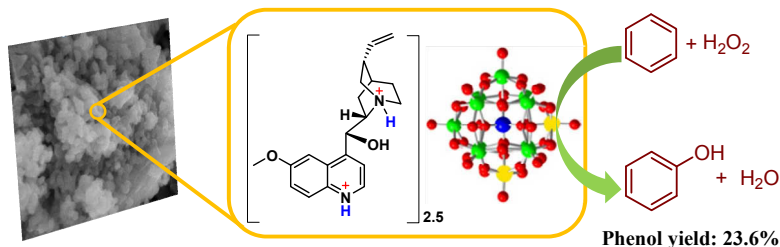
A quinine-modified phosphovanadomolybdate hybrid is developed as a heterogeneous catalyst for hydroxylation of benzene. The redox properties of the heteropolyanion are improved by quinine, accounting for its excellent catalytic performance.

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