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The Hydroxylation of Aromatics with Oxygen by Vanadium Catalysts Supported on N-doped Carbon Materials

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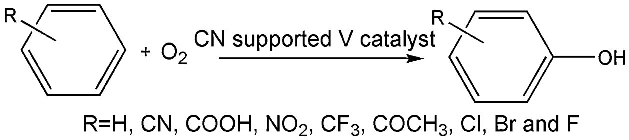
Abstract Vanadium catalysts supported on N-doped carbon materials (CN) were prepared and the catalyst VOSiW showed high activity for the hydroxylation of various aromatics with O_2. Aromatics with electron-withdrawing groups such as CN, NO_2, COOH, CF_3, $COCH_3$ and aromatic halides (F, Cl and Br) were oxygenated to the corresponding phenols in considerable yields. The CN materials were not only indispensable for the reusability of the vanadium catalyst VOSiW, but also favorable to the high catalytic activity. The VOSiW catalyst is ready for the hydroxylation of aromatics with O_2 as both V^{4+} and V^{5+} species are coexisted in the VOSiW catalyst.

Graphical Abstract



Keywords Hydroxylation · Phenol · Oxygen · Vanadium · Aromatics

1 Introduction

The activation of C–H bond is the most important research area in both fundamental and applied chemistry [1, 2]. The (C(sp2)–H/C(sp3)–H/) bonds are thermodynamically strong and kinetically inert, and the activation of the C–H bonds by conventional catalytic processes needs harsh reaction conditions [3, 4]. As phenol is currently produced by multistep processes with equivalent acetone as side-product, the direct hydroxylation of benzene to phenol with green oxidants (H_2O_2, O_2) has attracted much attention. Direct activation of C–H bonds of benzene, the hydroxylation of benzene to phenol with H_2O_2 was developed, which avoided acetone as side-product. In the view of green catalytic oxidation process, the use of inexpensive and abundant molecular oxygen as the oxidant is highly preferred [5, 6]. Thereafter, much attention has been paid to the hydroxylation of benzene to phenol with O_2. Among them, the polyoxometalates (POMs) have been widely studied due to their controllable redox and acidic properties [7–10]. Yamaguchi et al. [11] reported the liquid-phase oxidation of benzene in aqueous acetic acid solvent over vanadium (V) substituted heteropolyacids using O_2 as the oxidant and ascorbic acid as the reducing reagent, phenol was exclusively obtained as the product. Tani et al. [12] developed the direct synthetic method of producing phenol from benzene with air in the presence of carbon monoxide by molybdovanadophosphoric acid, which gave phenol in 26.9 % yield. We have reported a dual-catalysis system of carbon nitride (C_3N_4) with double-V substituted heteropolyacids as catalysts, which showed an exceptional activity for the hydroxylation of benzene to phenol [13]. Besides, we have also reported an organic–inorganic hybrid catalyst, which was prepared by combining bipyridine with single-V substituted heteropolyacids. The catalyst showed a relatively high phenol yield of 7.8 with 100 % selectivity by molecular oxygen [14].

Although the hydroxylation of benzene to phenol has been investigated extensively, most of the catalyst systems

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were limited to benzene, the substituted benzenes were not applicable for the hydroxylation. Photocatalytic oxidation of substituted aromatic compounds was reported, but the efficiency was not high enough [15, 16]. Phenols with one or more functional groups are valuable organic intermediates related to resins, plastics, pharmaceuticals, and agrochemicals in the chemical industry [17–20]. Recently, the hydroxylation of substituted benzenes to the corresponding phenols with H_2O_2 was reported using divanadium-substituted phosphotungstate as catalyst, but the catalyst system was still limited to the benzenes with electron-donor groups [17]. It is still a demanding challenge to the hydroxylation of benzenes with electron-withdrawing groups. The benzenes with F, Cl, Br and NO_2 have been oxidized to the corresponding monophenols by H_2O_2 with the vanadium peroxocomplexes, however, the conversion of the substrate was low (<3 %) [21]. Lei et al. [22] reported the Cu-catalyzed hydroxylation of electron-deficient arenes with air in the presence of NaOtBu. The ketone-directed Pd-catalyzed hydroxylation of aryl ketones had been reported and the catalyst exclusively activate the *ortho*-position [23]. The Pd-catalyzed *ortho*-hydroxylation of benzoic acids with molecular oxygen was developed with high selectivity and good yields [24]. Moreover, the *ortho*-hydroxylation of nitrobenzene to the *ortho*-nitrophenol with molecular oxygen using $H_5PMo_{10}V_2O_{40}$ POM catalyst was developed, and the formation of a $H_5PMo_{10}V_2O_{40}$–nitrobenzene complex was stated to be responsible for the *ortho*-hydroxylation [25]. However, all the catalyst systems were applicable with limited substrates, and the development of catalysts applicable widely for the hydroxylation of aromatics is still highly desirable.

Recently, we reported the SiO_2 encapsulated $H_5PMo_{10}V_2O_{40}$ POM catalyst, which was reusable and highly active and selective for the hydroxylation of benzene with hydrogen peroxide [26]. And we are still seeking immobilized catalysts for the hydroxylation of aromatics. Lately, molecularly defined Fe and Co complexes with N contained ligands were doped in activated carbon by pyrolysis as heterogeneous catalysts for the hydrogenation and oxidation reactions [27–29]. The ligand 1,10-phenanthroline can be linked into the surface of the activated carbon through pyrolysis of the complexes with 1,10-phenanthroline, and they were highly stable and were used as excellent supports for metal oxides. Moreover, the pyrolysis of protonated 1,10-phenanthroline gave a quite stable N-doped carbon material, which maybe used as a good support for catalysts [30]. Here, vanadium catalysts supported on N-doped carbon materials are reported as catalysts for the hydroxylation of functional aromatics to the corresponding phenols with O_2. It is widely applicable for the VOSiW catalyzed hydroxylation of aromatics, and various benzenes with electron-withdrawing groups such as CN, NO_2, COOH, CF_3, and $COCH_3$ are applicable for the hydroxylation with O_2. Aromatic halides (F, Cl and Br) can also be oxygenated to the corresponding phenols (see Scheme 1). The catalyst VOSiW was characterized by Fourier transform infrared spectra (FT-IR), X-ray diffraction (XRD) and electron spin resonance (ESR), which provided some information for the catalyst structure with the catalytic reactivity.

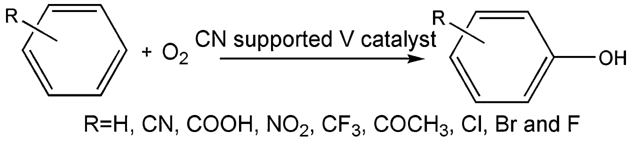
2 Experimental Section

2.1 Materials and Methods

All reagents were purchased from Aladdin Reagent Company, Sigma–Aldrich Company and Alfa-Aesar Company without further purification. $H_3PW_{12}O_{40}$ (PW), $H_3PMo_{12}O_{40}$ (PMo) and $H_4SiW_{12}O_{40}$ (SiW), purchased commercially, were dried before used. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 360 FT-IR instrument (KBr discs) in the 4,000–400 cm^{-1} region. XRD patterns were collected on the Bruker D8 Advance powder diffractometer using Ni–filtered Cu Kα radiation source at 40 kV and 20 mA, from 5° to 80° with a scan rate of 0.5°/min. BET surface areas were measured at the temperature of liquid nitrogen using a Micromeritics ASAP2010 analyzer. The samples were degassed at 150 °C to vacuum of 10^{-3} Torr before analysis. The amount of vanadium species was measured using a Jarrell-Ash 1100 inductively coupled plasma–atomic emission spectrometry (ICP–AES spectrometer). ESR spectra were recorded on a Bruker EMX-10/12 spectrometer at the X-band. Thermogravimetry (TG) analysis was carried out with a STA409 instrument under dry air at a heating rate of 10 °C/min. Elemental analyses were performed on a CHN elemental analyzer (FlashEA 1112).

2.2 Catalyst Preparation

$H_3PW_{12}O_{40}$ (1.44 g, 0.5 mmol) and vanadium oxytrichloride oxide ($VOCl_3$, 0.086 g, 0.5 mmol) were dissolved in absolute ethyl alcohol (20 mL) under argon atmosphere with stirring for 6 h. 1,10-Phenanthroline hydrate (0.3 g, 1.5 mmol) was dissolved in 10 mL absolute ethyl alcohol,



Scheme 1 The hydroxylation of substituted aromatic compounds with O_2

and the solution was added drop-wise to the above mixture with the appearance of precipitate, and then the mixture was stirred at room temperature for 24 h. The solvent was removed by evaporation under vacuum and the catalyst precursor designated as VOPW-p. VOPW-p (1.5 g) was transferred into a crucible and heated in a tube furnace under Ar at a rate of 5 °C/min to reach the temperature of 500 °C and kept at 500 °C for 4 h, and then the resulting black sample (1.45 g) was cooled to room temperature under Ar. The black catalyst was denoted as VOPW. VOPMo and VOSiW were prepared accordingly by using $H_3PMo_{12}O_{40}$ (PMo) and $H_4SiW_{12}O_{40}$ (SiW). VPW, VPMo and VSiW were prepared accordingly by using vanadium chloride (VCl_3) instead of vanadium oxytrichloride oxide ($VOCl_3$).

2.2.1 $H_5PMo_{10}V_2O_{40}$ (PMoV)

The double vanadium-containing POM was prepared according to the procedure described in our previous report [26]. The detail of the preparation of PMoV is as the following. MoO_3 (16.59 g) and V_2O_5 (2.1 g) were added to deionized water (250 mL). The mixture was heated up to the reflux temperature under vigorously stirring with a water-cooled condenser, then at 120 °C the 85 % aqueous solution of H_3PO_4 (1.33 g) was added drop-wise to the reaction mixture. When a clear orange–red solution appeared, it was cooled to room temperature. The orange–red powder PMoV was obtained by evaporation of the solution to dryness, followed with re-crystallizing for purification.

3 Results and Discussions

3.1 Catalyst Characterization

The catalyst VOSiW was characterized by FT-IR, XRD and ESR. Figure 1 illustrates the IR spectra for $H_4SiW_{12}O_{40}$ (SiW), VOSiW-p and VOSiW. As shown in Fig. 1a, four characteristic bands for Keggin structure at 1,070, 965, 870 and 790 cm^{-1} are remained for SiW, which assignable to ν(Si–O_a), ν(W–O_t) (terminal oxygen), ν(W–O_b–W) (corner-sharping oxygen), and ν(W–O_c–W) (edge-sharping oxygen), respectively. And the structure of SiW was reserved in the VOSiW catalyst [31]. The new weak IR bands between 1,500 and 1,000, 2,500 and 2,000 cm^{-1} appeared for the CN material with structure of 1,10-phenanthroline in the AC (Fig. 1b) [32].

XRD patterns of SiW, VOSiW-p and VOSiW are shown in Fig. 2. Pure SiW presented a set of diffraction peaks for the triclinic crystal structure of the Keggin-type HPA. However, no obvious peak was found in the pre-catalyst VOSiW-p and catalyst VOSiW, which indicates the formation of new three dimension structures assembled by Keggin anions with 1,10-phenanthroline [33]. As can be seen in Fig. 2c, there is a broadening diffraction peak at ca. 27°, reflections characteristic for graphitic structures [34]. Figure 3 shows the ESR spectra of the fresh catalyst VOSiW and the recycled catalyst. The signals are sharp and strong, which suggest the coexistence of V^{4+} and V^{5+} species in the catalyst VOSiW [35–38]. The coexistence of V^{4+} and V^{5+} species in the catalyst is important for the hydroxylation of benzene with O_2 [39–41]. The elemental analysis for VOSiW found C 7.9 %; H 0.4 %; N 0.9 % by weight percentage, which is consistent with the TG analysis (Fig. 4). Although the contents of C and N in the catalysts are low, it is indispensable for the immobilization of the POM catalysts, and responsible for the high activities in the oxygenation of aromatics [42, 43].

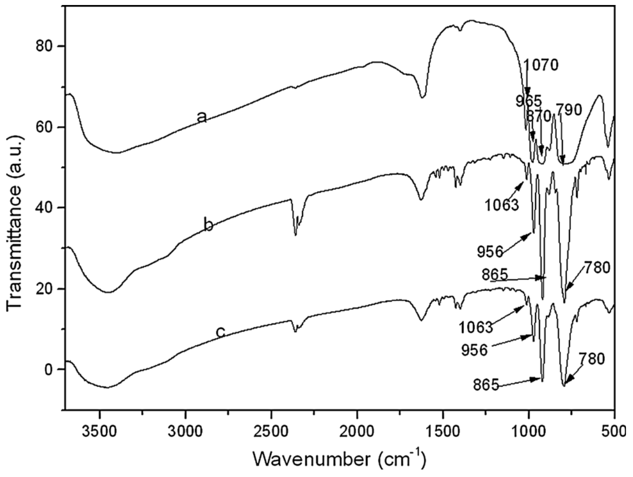


Fig. 1 FT-IR spectra of *a* $H_4SiW_{12}O_{40}$, *b* VOSiW-p (precursor of the VOSiW before calcination) and *c* VOSiW

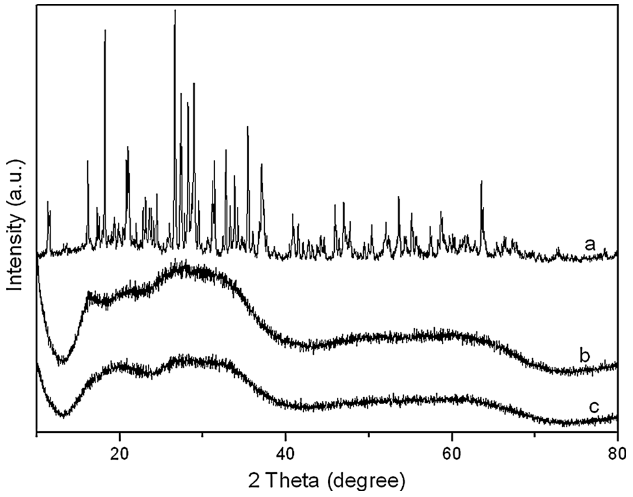


Fig. 2 XRD spectra of *a* $H_4SiW_{12}O_{40}$, *b* VOSiW-p and *c* VOSiW

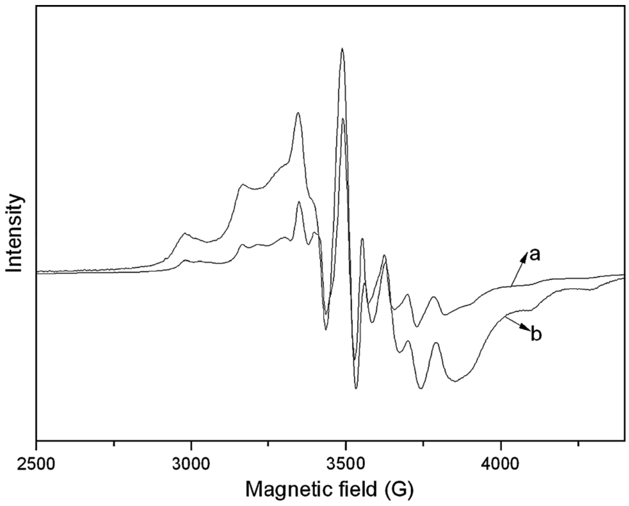


Fig. 3 ESR spectra of *a* fresh VOSiW and *b* recycled VOSiW

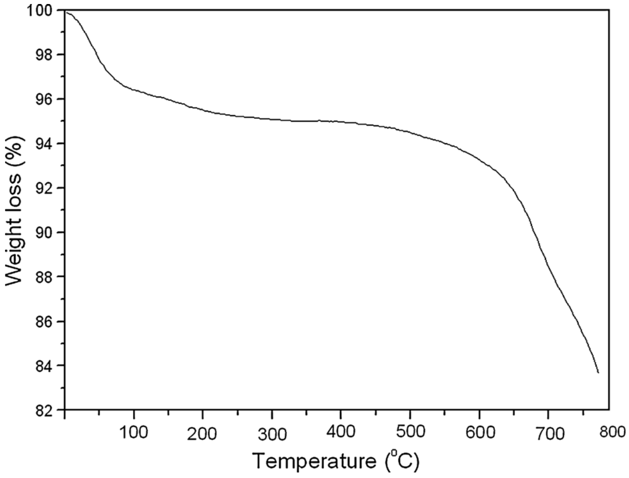


Fig. 4 TG analysis of the precursor VOSiW-p

3.2 The Hydroxylation of Benzene to Phenol Under Different Conditions

The catalytic performance of V contained catalysts for the hydroxylation of benzene to phenol was investigated using molecular oxygen as the oxidant, and the results are listed in Table 1. When no catalyst (no ascorbic acid also) was added into the reaction, no phenol obtained (Table 1, entry 1). The vanadium-free heteropolyacid SiW and $H_3PMo_{12}O_{40}$ (PMo) were not active, and phenol was obtained in low yield (4 and 4 % respectively) (Table 1, entry 2, 3). The double vanadium-containing heteropolyacid $H_5PMo_{10}V_2O_{40}$ was active, and phenol was obtained in 13 % yield (Table 1, entry 4). The catalyst VOSiW was much more active, and phenol was obtained in 18.3 % yield (Table 1, entry 5). The precursor VOSiW-p was also active for the hydroxylation (18 % yield, Table 1, entry 6), but the VOSiW-p was soluble in the reaction system. To test the role of added SiW in the VOSiW catalyst, the catalyst VOPhen (pyrolysis of the the mixture of $VOCl_3$ and 1,10-phen-anthroline) was examined, and the VOPhen was not as active as the VOSiW catalyst (8 % yield Table 1, entry 7). When ascorbic acid added to 1.5 equivalent of benzene, and phenol was obtained in 27 % yield (Table 1, entries 8). When the Keggin-structured silicotungstic acid anion was replaced by phosphotungstic acid (PW) and phosphomolybdic acid (PMo), the catalysts (VOPW, VOPMo) were also active for the hydroxylation of benzene to phenol with O_2, and phenol was obtained in considerable yields (Table 1, entries 9, 10). Notably, the phenol was the only product, and no by-product was detected in the hydroxylation reaction mixtures.

Table 1 The hydroxylation of benzene to phenol under different conditions

Entry	Catalyst	Conv.%	Phenol yield (%)
1	None	0	0
2	SiW	4	4
3	PMo	4	4
4	$H_5PMo_{10}V_2O_{40}$	13	12
5	VOSiW	18	18
6	VOSiW-p	18	18
7	VOPhen[a]	8	8
8[c]	VOSiW	27	27
9[b,c]	VOPW	26	26
10[c,d]	VOPMo	26	26

Reaction conditions: benzene (1 mmol); catalyst (0.013 mmol V); O_2 (1.5 MPa); water (5 mL); acetic acid (5 mL); ascorbic acid (0.15 mmol); 105 °C; 11 h

[a] The catalyst prepared by pyrolysis of the the mixture of $VOCl_3$ and 1,10-phenanthroline dried from ethanol solution

[b] VOPW and VOPMo prepared similar to the catalyst VOSiW

[c] Ascorbic acid 1.5 mmol added

3.3 Influences of Reaction Conditions

The effect of the catalyst amount on the phenol yield over VOSiW is shown in Fig. 5. The phenol yield increased with the increasing of catalyst loading up to 50 mg (0.013 mmol V). However, further increasing the catalyst amount had a reverse effect on the phenol yield, which was due to the over oxidation of the phenol to coke. Therefore, 50 mg (0.013 mmol V) is the optimized catalyst amount.

Solvent plays an important role in the direct hydroxylation of benzene to phenol, especially with molecular oxygen as the oxidant. Among the solvents, H_2O is the most environmentally benign. But the substrate, benzene is insoluble in H_2O, which reduced the contact opportunities of the oxidant (O_2) with the substrate (benzene). As shown

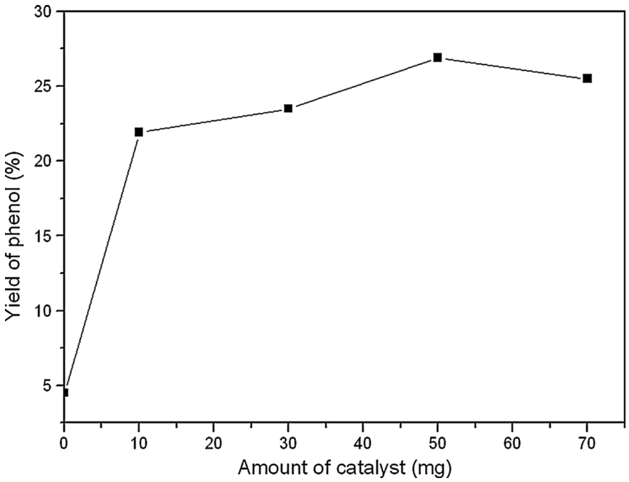


Fig. 5 Influence of catalyst amount on phenol yield in VOSiW catalyzed hydroxylation of benzene with oxygen molecular. Reaction conditions: benzene (1 mmol); ascorbic acid (1.5 mmol); O_2 (1.5 MPa); water (5 mL); acetic acid (5 mL); 105 °C; 11 h

in Fig. 6, only 4.5 % of phenol was obtained when H_2O alone as the solvent. It has been reported that an appropriate acidity is vital for the hydroxylation of benzene to phenol. Furthermore, the addition of acetic acid can enhance the solubility of benzene. The maximum yield (26.9 %) is achieved at the acetic acid concentration of 50 %. However, a much higher concentrations of acetic acid gave a lower yield of phenol. Moreover, the phenol yield is only 5.1 % by using pure acetic acid. In the end, the optimized concentration of acetic acid was 50 %.

The effect of reaction time on the catalytic activity of VOSiW under the above optimal conditions is presented in Fig. 7. The phenol yield of 25.3 % was detected at the early reaction period within 9 h. However, when the reaction time was elongated to 11 h, the phenol yield continue to grow but at a more moderate pace. When the reaction time was elongated to 16 h, it appears to have contrary effect on phenol yields. Therefore, 11 h was considered as the optimized reaction time.

3.4 The Scope and Limitation

With the optimized reaction conditions in hand, we tried to extend the hydroxylation reaction to substituted aromatics, and the results are shown in Table 2. To our delight, the hydroxylation of aromatic halides gave to the corresponding phenols in good yield (15–33 %) with the distribution of isomers of *ortho*-(*o*) and *para*-(*p*), and no by-products were detected. But the *para*-substituted phenols were produced preferentially for the hydroxylation of aromatic halides (Table 2, entries 1–3). Benzotrifluoride can be transformed to the trifluoromethylphenol (distributed in *o*-, *m*- and *p*-) in 13 % yield (Table 2, entry 4). Moreover, the hydroxylation of aromatics with electron-withdrawing groups such as acetophenone, benzonitrile, benzoic acid and nitrobenzene also afforded the corresponding phenols in good yields without by-products (Table 2, entries 5–9). And the hydroxylation occurred preferably at the *ortho*-position for the aromatics with electron-withdrawing groups such as acetophenone, benzonitrile, benzoic acid and nitrobenzene, and the *ortho*-hydroxylated products were obtained higher than other isomers (*m*-/*p*-hydroxylated products) (Table 2, entries 5–9). The hydroxylation of *p*-terephthalonitrile with two electron withdrawing groups gave 2-hydroxyterephthalonitrile in 5 % yield. It is interesting that the catalyst VOSiW was completely

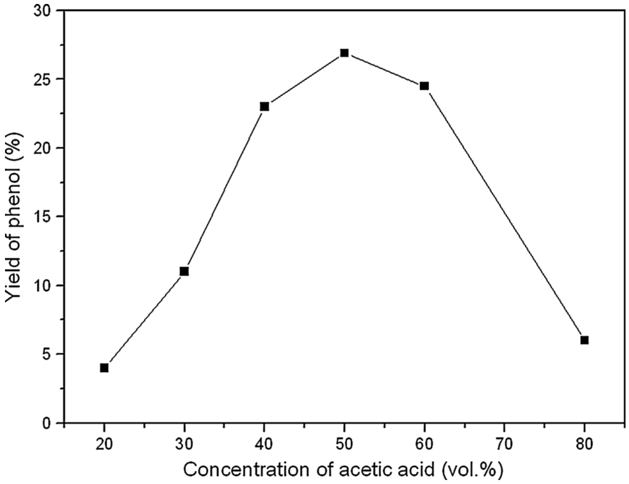


Fig. 6 Influence of concentration of acetic acid on phenol yields in VOSiW catalyzed hydroxylation of benzene with oxygen molecular. Reaction conditions: benzene (1 mmol); catalyst VOSiW (50 mg, 0.013 mmol V); ascorbic acid (1.5 mmol); O_2 (1.5 MPa); solvent (acetic acid and water, 10 mL); 105 °C; 11 h

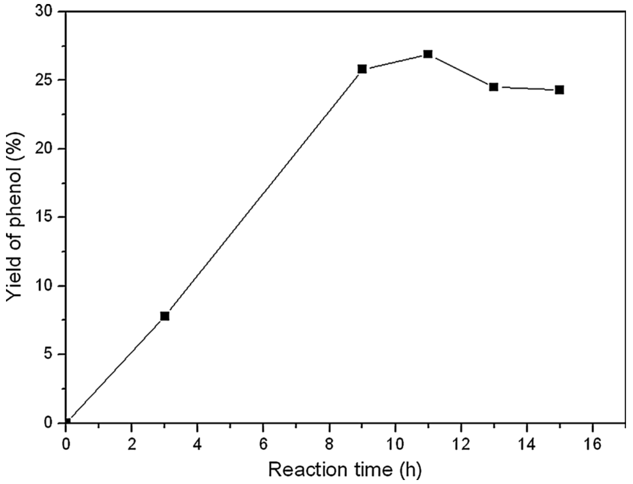
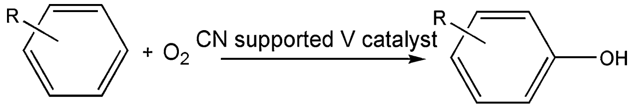
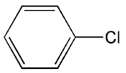
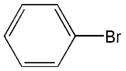
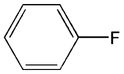
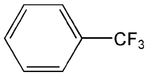
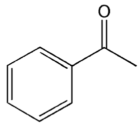
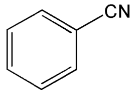
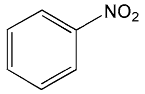
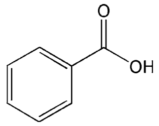
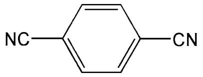
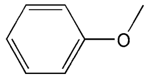
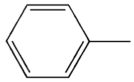


Fig. 7 Influence of reaction time on phenol yields in VOSiW catalyzed hydroxylation of benzene with oxygen molecular. Reaction conditions: benzene (1 mmol); catalyst (50 mg, 0.013 mmol V); ascorbic acid (1.5 mmol); O_2 (1.5 MPa); water (5 mL); acetic acid (5 mL); 105 °C

Table 2 Hydroxylation of arenes to phenols with O_2 catalyzed by VOSiW



R=H, CN, COOH, NO_2, CF_3, $COCH_3$, Cl, Br and F

Entry	Substrate	Yield (%)	Selectivity (%)
1		33	*o*/*m*/*p* = 32/0/68
2		21	*o*/*m*/*p* = 37/0/63
3		15	*o*/*m*/*p* = 35/0/65
4		13	*o*/*m*/*p* = 31/46/23
5		24	*o*/*m*/*p* = 53/26/21
6		22	*o*/*m*/*p* = 45/23/32
7		15	*o*/*m*/*p* = 43/31/26
8		30	*o*/*m*/*p* = 43/37/20
9		5	2-Hydroxy terephthalonitrile
10		0	–
11		26	Benzaldehyde

Reaction conditions: substrate (1 mmol); catalyst VOSiW (50 mg, 0.013 mmol V); ascorbic acid (1.5 mmol); O_2 (1.5 MPa); water (5 mL); acetic acid (5 mL); 105 °C; 11 h

inactive for the hydroxylation of anisole, and no conversion was found when anisole used as the substrate (Table 2, entry 10). In the case of benzene ring with methyl group, the oxidation took place at the methyl group, giving benzaldehydes in 26 % yield (Table 2, entry 11).

3.5 Catalyst Reusability

The VOSiW was a heterogeneous catalyst, and the VOSiW can be recovered easily by centrifugation. The recovered VOSiW catalyst was used again for the hydroxylation of benzene with O_2 under the same reaction conditions. And the reusability of the VOSiW catalyst was tested for the hydroxylation of benzene with O_2, and the results are shown in Fig. 8. As shown in Fig. 8, at the six runs reaction, phenol was obtained in 20 % yield, suggesting that the catalysts can be recycled at least six times without obvious loss of activity. In order to test the leak of the catalyst (vanadium species), we measured the content of the catalyst (vanadium species) recovered from the 6th time reaction by ICP-AES, and the vanadium was leaked about 8 % after 6 reaction cycles.

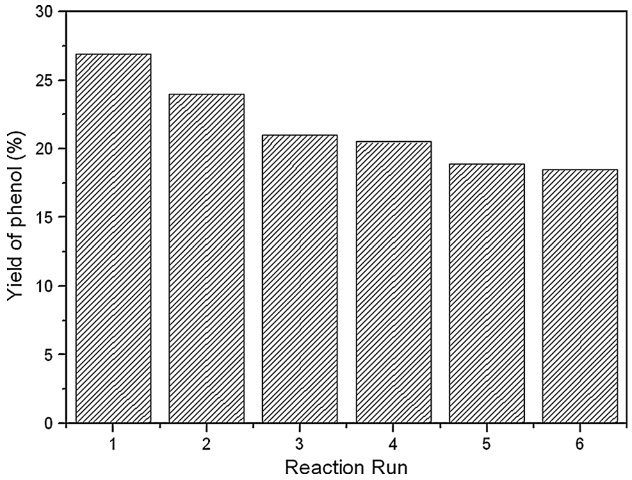


Fig. 8 Catalytic reusability of VOSiW for hydroxylation of benzene to phenol. Reaction conditions: benzene (1 mmol); catalyst (50 mg, 0.013 mmol V); ascorbic acid (1.5 mmol); O_2 (1.5 MPa); water (5 mL); acetic acid (5 mL); 105 °C; 11 h

3.6 Catalysis Mechanism Discussion

The vanadium species is a key element for the VOSiW catalyzed hydroxylation of benzene, although the active species is not identified definitely. Some insights into the mechanism were presented for the hydroxylation. Since H_2O_2 is reported to be good oxidant for the hydroxylation of benzene with $H_5PMo_{10}V_2O_{40}$, we examined the hydroxylation of benzene by VOSiW catalyst with H_2O_2. We found O_2 was emitted quickly even at room temperature, and no phenol was obtained, which indicated that the H_2O_2 decomposed into O_2 and water quickly. And the hydroxylation was not through the way of H_2O_2. With O_2 as oxidant, the VOSiW catalyst was more active than $H_5PMo_{10}V_2O_{40}$ (Table 1, entries 4, 8), which indicated that the V species in VOSiW and in $H_5PMo_{10}V_2O_{40}$ were in different states respectively. In VOSiW catalyst, the V species is coordinated by N (N from the linked phen) and O (O from POMs anions), which is different from the V species in $H_5PMo_{10}V_2O_{40}$ (all coordinated with O). In order to obtain insights to the mechanism of the VOSiW catalyzed hydroxylation of benzene to phenol by O_2, several control experiments were performed. Firstly, the hydroxylation of benzene (1 mmol) with O_2 (1.5 MPa) by VOSiW (0.26 mmol V contained) in the absence of ascorbic acid was carried out. Trace of phenol was detected. When the catalyst VOSiW (0.26 mmol V^{4+}) was treated with ascorbic acid (3 mmol), and then the hydroxylation gave 0.07 mmol of phenol under similar reaction conditions, which implied that the V^{4+} species was the active center (1 mmol benzene; 1.5 Mpa O_2; in the absence of ascorbic acid). Moreover, the hydroxylation gave trace of phenol using VOSiW (0.26 mmol V^{5+}; treated with H_2O_2) under similar reaction conditions (1 mmol benzene; 1.5 Mpa O_2; in the absence of ascorbic acid), and the V^{5+} species was not the active center for the hydroxylation. Based on these results, the hydroxylation pathway was proposed. The V^{4+} species may react with O_2 to generate an activated peroxide intermediate species V^{5+}–O_2. Immediately, the formed species V^{5+}–O_2 attacked the substrates to produce the corresponding phenols and released the V^{5+} species. Finally, the V^{5+} species was reduced to the V^{4+} state by ascorbic acid and the catalytic cycle was finished. And ESR spectra showed the coexistence of V^{4+} and V^{5+} species (in fresh or recycled VOSiW), which implied that the VOSiW was ready for the hydroxylation, and that was in agreement with the proposed pathway.

4 Conclusions

In conclusion, CN supported vanadium catalysts were prepared and the catalysts showed unique activity for the hydroxylation of functional aromatics with O_2. Aromatics with electron-withdrawing groups such as CN, NO_2, COOH, CF_3, $COCH_3$ and aromatic halides (F, Cl and Br) were transformed to the corresponding phenols in considerable yields. The CN material was not only indispensable for the reusability of the VOSiW catalyst, but also favorable for the high activity. The VOSiW catalyst is ready for the hydroxylation of aromatics with O_2 as both V^{4+} and V^{5+} species are coexisted in VOSiW catalyst. Although the regioselectivity of the hydroxylation was not good, the VOSiW catalyst exhibited the potential of the V as active center for the activation of C–H bonds and the activation of O_2.

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