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Article

Direct hydroxylation of arenes with O_2 catalyzed by V@CN catalyst

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ABSTRACT

A vanadium doped graphitic carbon nitride catalyst has been prepared and used for the direct hydroxylation of arenes with O_2. Substituted arenes with electron-withdrawing groups such as CN, NO_2, COOH, CF_3, and $COCH_3$ were oxygenated to the corresponding phenols in moderate yields. The catalyst also proved applicable for the hydroxylation of aromatic halides (F, Cl, and Br) with O_2.

1. Introduction

The direct introduction of hydroxy groups into arenes is an important process in both fundamental and applied chemistry across a wide variety of fields ranging from resins and plastics to agrochemicals and pharmaceuticals [1]. Traditionally, phenols with one or more functional groups have been produced industrially in multistep processes. The direct hydroxylation of arenes to phenols would therefore be a great improvement and attracts much attention despite being a challenging subject [2,3]. To meet the needs of a green catalytic process, environmentally-friendly oxidants (such as H_2O_2 [4–12], N_2O [13,14], and O_2 [15,16]) have been investigated for the hydroxylation of arenes to phenols. Vanadium complexes are active towards the oxidation of a hydrocarbon with O_2, H_2O_2, and other oxygen donors [17–20]. As O_2 is abundant and cheap, many investigations have targeted efficient catalysts for the hydroxylation of benzene to phenol that can use molecular oxygen as the oxidant [21–26]. However, the hydroxylation reaction has been limited to the hydroxylation of benzene to phenol, and few reports have been made on the hydroxylation of arenes containing functional groups. Using H_2O_2 as oxidant, the hydroxylation of arenes with one or more substitutes has been achieved with a divanadium-substituted phosphotungstate catalyst under extreme reaction conditions, using a molar ratio of arene to H_2O_2 of 50:1 [27]. However, the reaction system was limited to the arenes with electron-donating groups. Some substituted 2-phenylpyridines have been regioselectively oxidized to the substituted 2-(pyridin-2-yl)phenols when catalyzed by $PdCl_2$ and using N-hydroxyphthalimide (NHPI) and O_2 [28]. However, both the noble metal Pd catalyst and NHPI are expensive and are required for the hydroxylation. Pd-catalyzed *ortho*-hydroxylation of benzoic acids has also been developed [29]. Oxygenase has been used in the oxidation of arenes, with the hydroxylation of electron-deficient arenes being carried out at room temperature under air [30], but an excess strong base was

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used. $H_5PMo_{10}V_2O_{40}$ has been found to be active for the ortho-hydroxylation of nitrobenzene with molecular oxygen, although the activity was low [31]. The hydroxylation of arenes remains limited when functional groups are present. Recently, we reported on immobilized polyoxometalate catalysts containing vanadium, which were reusable and highly active for the selective hydroxylation of benzene [32,33].

More recently, there has been growing interest in the use of carbon nitrides. Mesoporous carbon nitride (mpg-C_3N_4) is predicted to be the most stable allotrope in ambient conditions, and numerous articles have been published on the synthesis of mpg-C_3N_4 and its derivatives [34–36]. mpg-C_3N_4 can be directly used for oxidation [37–39] and Friedel-Crafts reactions [40]. Moreover, metal doped mpg-C_3N_4 has been explored for use as catalysts [41,42]. V@mpg-C_3N_4 was found to be highly active in the hydroxylation of benzene to phenol [43,44]. Based on these results, a vanadium-doped graphitic carbon nitride (V@CN) catalyst was prepared using dicyandiamide as the carbon nitride source and vanadiumoxy acetylacetonate as the vanadium precursor. V@CN was investigated for the direct hydroxylation of functional arenes using O_2. Benzenes with electron-withdrawing groups such as CN, NO_2, COOH, CF_3, and $COCH_3$ were oxygenated to the corresponding phenols. The catalyst was also tested for applicability for the hydroxylation of aromatic halides (F, Cl, and Br).

2. Experimental

2.1. General methods and reagents

All reagents were purchased from the Aladdin Reagent Company, Sigma-Aldrich Company, and Alfa-Aesar Company and used without further purification. X-ray diffraction (XRD) patterns were collected on the Bruker D8 Advance powder diffractometer using Ni-filtered Cu K_α radiation source at 40 kV and 20 mA, from 5° to 80° at a scan rate of 0.5°/min. The BET surface areas were measured at −196 °C with liquid nitrogen using a Micromeritics ASAP 2010 analyzer. The samples were degassed at 150 °C under a vacuum of 10^{-3} Torr before analysis. The CHN elemental analysis (EA) was performed on an elemental analyzer Vario EL cube. Thermogravimetric (TG) analysis was carried out with a STA409 instrument under dry air at a heating rate of 10°C/min. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al K_α radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C 1*s* line at 284.8 eV from adventitious carbon. ESR spectra were recorded on a Bruker EMX-10/12 spectrometer at the X-band. The amount of vanadium species was measured using a Jarrell-Ash 1100 ICP-AES spectrometer (inductively coupled plasma-atomic emission spectrometry).

2.2. Preparation of catalysts

Dicyandiamide (3.0 g, 35.7 mmol) and vanadiumoxy acetylacetonate (0.3 g, 1.1 mmol) were dissolved in 200 mL of absolute ethanol with stirring at 50 °C for 12 h. The solvent was removed by rotary evaporation and a white solid was obtained. The solid was transferred into a tube furnace and heated to 150 °C under a flow of N_2, and then heated to 550 °C at a rate of 4 °C/min and kept at 550 °C for 4 h. The resulting black powder (V@CN) was cooled to room temperature under N_2. Other metal doped CN catalysts, including Cu@CN, Fe^{III}@CN, and Fe^{II}@CN were synthesized in a similar process. The metal precursors used for preparing these catalysts were cupric(II) acetylacetonate, iron(III) acetylacetonate, and iron(II) acetylacetonate, respectively.

2.3. Typical procedure for aromatics hydroxylation with O_2

Hydroxylation reactions of aromatics to the corresponding phenols were carried out in a 50-mL stainless steel autoclave with a Teflon liner and magnetic stirring. Typically, 10 mmol of the arene, 100 mg of V@CN (0.11 mmol V), 1.5 mmol of ascorbic acid, and 10 mL of aqueous acetic acid (50 vol%) were sealed in the autoclave. The autoclave was then flushed three times with O_2, pressurized with O_2 to 1.5 MPa, and transferred into 105 °C oil bath with stirring. The reactor was kept at this temperature for 11 h. After the reaction mixture was cooled to room temperature, dioxane (100 μL) was added to the mixture as an internal standard for product analysis. The mixture was analyzed by gas chromatography (GC). The yields of phenols were calculated as mmol phenol/mmol initial benzene.

After the reaction was finished, the reaction mixture was cooled to room temperature. The catalyst was separated by centrifugation and washed with diethyl ether three times. The obtained catalyst was then used directly for the next run.

3. Results and discussion

3.1. Catalyst characterization

V@CN and the catalyst precursor (the mixture of dicyandiamide and vanadiumoxy acetylacetonate) were analyzed by XRD (Fig. 1). A number of sharp Bragg peaks appeared for the catalyst precursor, which meant that it contained at least one

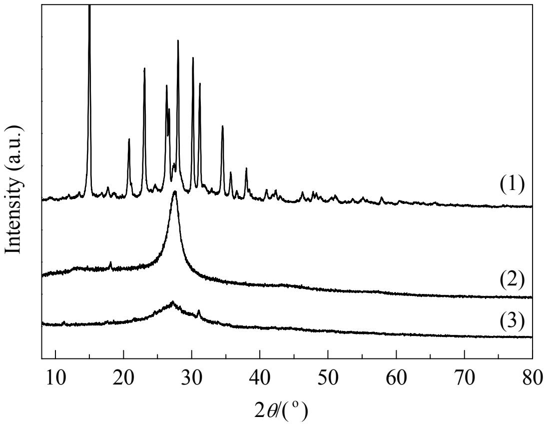


Fig. 1. XRD patterns of the mixture of dicyandiamide and vanadiumoxy acetylacetonate (1), recycled V@CN after four runs (2), and V@CN (3).

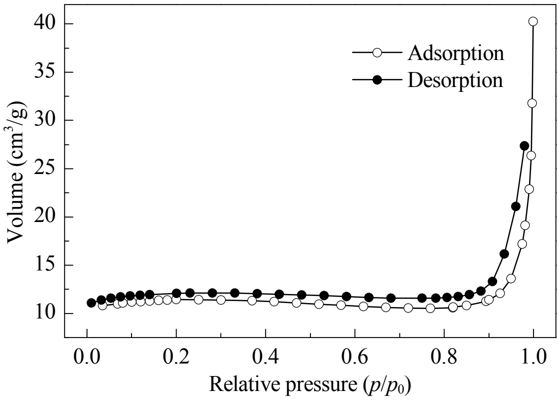


Fig. 2. N_2 adsorption-desorption isotherm of V@CN.

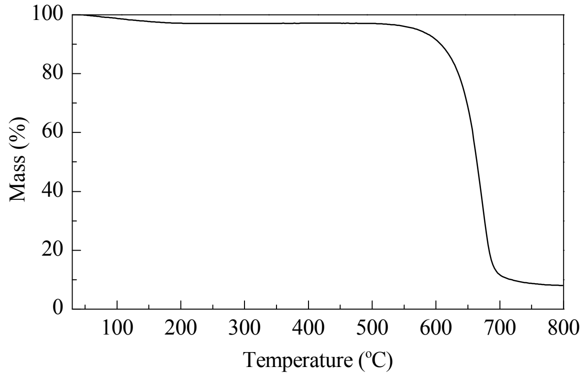


Fig. 3. TG curve of the catalyst V@CN.

crystalline phase. These peaks disappeared in V@CN, and a single broad peak at 2θ = 27.5° was observed. This was assigned to the interlayer diffraction from a graphitic structure [45,46]. There was no diffraction peak found for a vanadium species in V@CN, suggesting a lack of crystalline vanadium species in the carbon nitride material. These observations show that the vanadium was uniformly doped into the composite during the formation of a carbon nitride material. The N_2 adsorption-desorption isomer is shown in Fig. 2. V@CN had a BET surface area of about 18 m²/g. The EA results were consistent with graphitic carbon nitride (found: C, 26.86 wt%; H, 2.32 wt%; N, 32.33 wt%). Results from ICP-AES revealed that the amount of vanadium in the catalyst was 1.1 mmol/g (10 wt%), which was consistent with the TG result (Fig. 3).

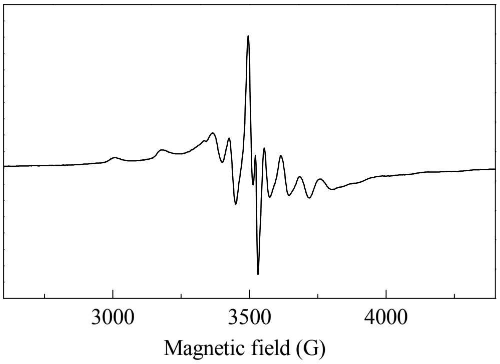


Fig. 5. ESR pattern of the catalyst V@CN.

To understand the surface composition of the catalyst, in particular the valence state of the vanadium, V@CN was characterized by XPS and ESR. Figure 4(a) shows the high resolution V 2*p* XPS spectrum. The two peaks centered at 524.5 and 517.6 eV corresponded to V $2p_{1/2}$ and V $2p_{3/2}$, suggesting the presence of a V^{5+} species. The other two peaks located at 523.4 and 514.9 eV corresponded to V $2p_{1/2}$ and V $2p_{3/2}$, indicating the presence of a V^{4+} species [47]. The C 1*s* spectrum (Fig. 4(b)) has two peaks at 284 and 287 eV. The peak at 284 eV is assigned to carbon bonded to other carbon atoms. The peak at 287 eV is attributed to carbon atoms bonded to three nitrogen atoms in the g-C_3N_4 lattice [47]. The XPS spectra of N 1*s* (Fig. 4(c)) showed two nitrogen species. The peak at 398.7 eV is attributed to nitrogen bonded to two carbon atoms (C–N–C). The peak at 399.8 eV is assigned to an amino functional groups [43]. To obtain more information on the valence state of the vanadium, the catalyst V@CN was also characterized by ESR. As shown in Fig. 5, the sharp and strong ESR signals for V@CN confirm again the coexistence of V^{5+} and V^{4+} species. The coexistence of V^{5+} and V^{4+} species may be highly useful for the hydroxylation of benzene. Generally, V^{4+} species can react with O_2 to generate active peroxide intermediate species V^{5+}–O_2 for the hydroxylation of benzene. After the hydroxylation, V^{5+} species are left, which need to be reduced back to V^{4+} species by the ascorbic acid.

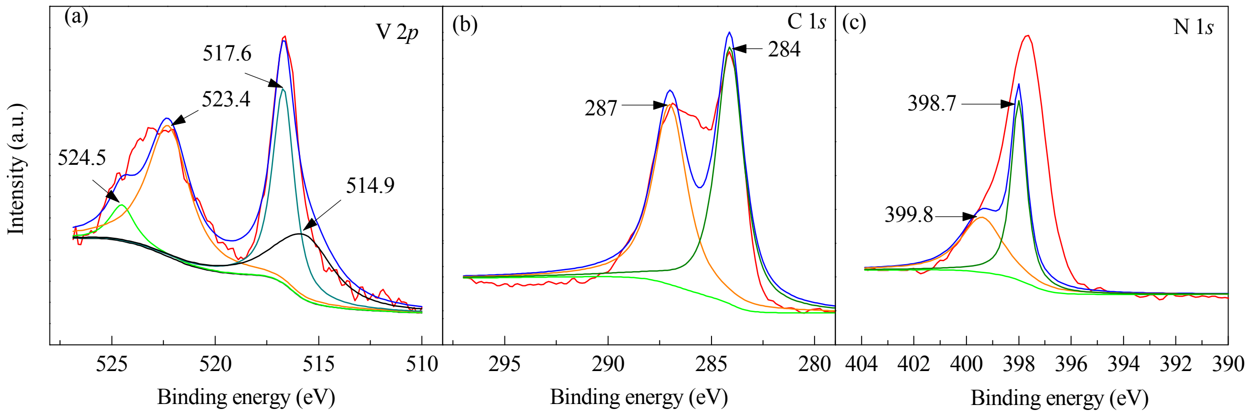


Fig. 4. High resolution V 2*p* (a), C 1*s* (b), and N 1*s* (c) XPS spectra and proposed deconvolution.

3.2. Reaction condition optimization

The optimization of the reaction conditions (including the amount of catalyst and ascorbic acid, acetic acid concentration, and reaction time) was performed and the results are shown in Fig. 6. The phenol yields (at 105 °C with 1.5 MPa O_2) were depended on the amount of catalyst, acetic acid concentration, amount of ascorbic acid, and reaction time. The optimized conditions are as follows: 100 mg of catalyst (0.11 mmol V), 1:1 of H_2O/acetic acid volumetric ratio (5 mL), 1.5 mmol of ascorbic acid, and an 11-h reaction.

Cu, Fe, and V based catalysts have been widely investigated for the hydroxylation of benzene to phenol with H_2O_2. Thereafter, we synthesized the Cu, Fe, and V doped carbon nitrides catalysts. These catalysts were tested for the hydroxylation of benzene to phenol with O_2. No phenol was obtained in the absence of catalyst and ascorbic acid (Table 1, entry 1). When 1.5 mmol ascorbic acid was added into the reaction, phenol was detected in 4.5% yield (Table 1, entry 2). The hydroxylation of benzene with metal-free CN also gave phenol in 4.3% yield in the absence of ascorbic acid (Table 1, entry 3). Cu^{II}, Fe^{II}, and Fe^{III} doped CN catalysts were found to be active for the direct hydroxylation of benzene to phenol (Table 1, entries 4–6) with the highest phenol yield of 16.9% using the Fe^{II}@CN catalyst (Table 1, entry 6). Compared with the other catalysts, under the same conditions, V@CN was much more active, and phenol was obtained in 23.0% yield (Table 1, entry 7). The results showed that V@CN was suitable for the direct hydroxylation of benzene to phenol with O_2. Additionally, homogeneous $VO(acac)_2$ was also active, and yielding phenol at 18.1%.

Table 1
The hydroxylation of benzene to phenol over various catalysts.

Entry	Catalyst	Conversion (%)	Phenol yield (%)
1	None	0	0
2	Ascorbic acid	4.5	4.5
3	CN *	4.3	4.3
4	Cu@CN	10.9	10.9
5	Fe^{III}@CN	10.6	10.6
6	Fe^{II}@CN	16.9	16.9
7	V@CN	23.0	23.0
8	$VO(acac)_2$	18.1	18.1

Reaction conditions: benzene (5 mmol), catalyst (0.11 mmol metal), ascorbic acid (1.5 mmol), H_2O (5 mL), acetic acid (5 mL), O_2 (1.5 MPa), 105 °C, 11 h. * 100 mg CN, without ascorbic acid.

3.3. Hydroxylation of arenes to phenols with O_2 catalyzed by V@CN

Because the hydroxylation of functional arenes has been only rarely reported, we tried to extend the hydroxylation reaction to functionalized arenes, especially those with electron-withdrawing groups. With the optimal reaction conditions, we examined the hydroxylation of a series of arenes using V@CN with O_2, and the results are listed in Table 2. Aryl halides such as the fluorobenzene, chlorobenzene, and bromobenzene were transformed into the corresponding phenols in moderate yields in a distribution of *ortho-* (*o*) and *para-* (*p*) isomers, and no detectable by-products (Table 2, entries 1–3). Moreover, no meta-substituted phenols were detected (Table 2, entries 1–3). Functional arenes with electron-withdrawing groups such as NO_2, CN, CH_3CO, CF_3, and COOH were also oxygenated to the

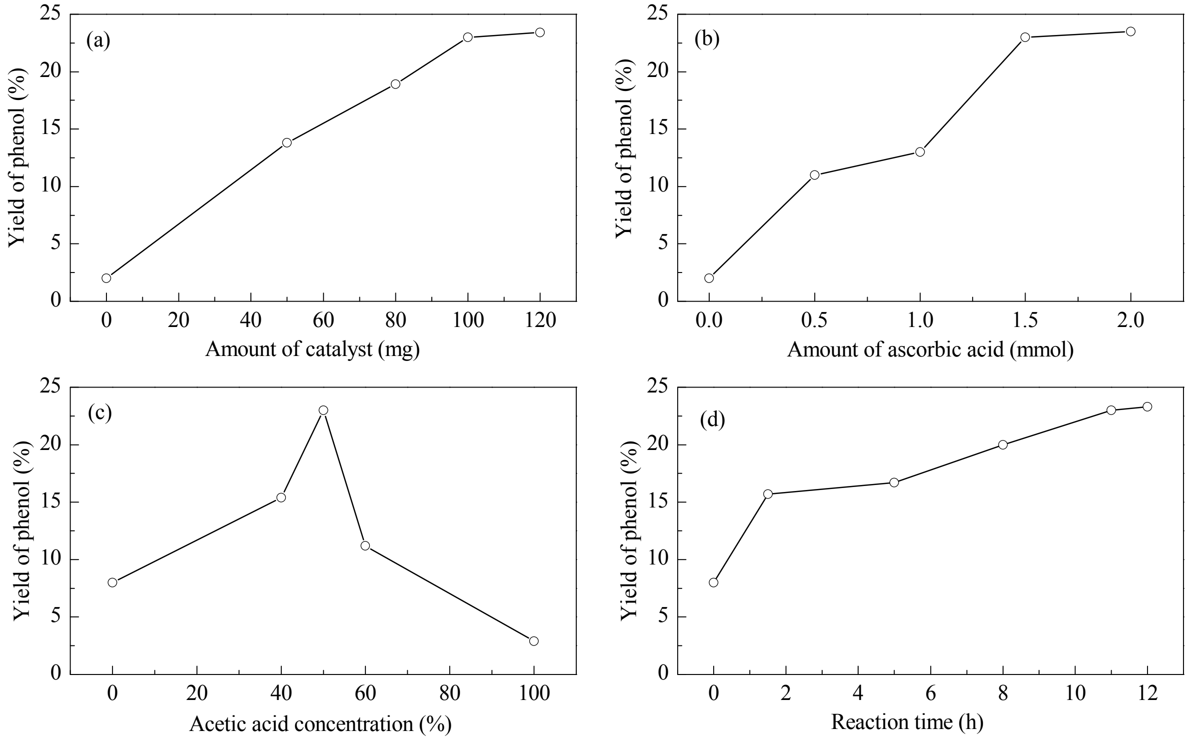
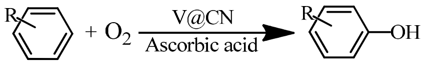
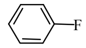
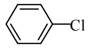
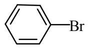
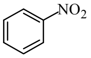
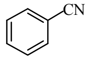
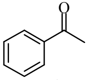
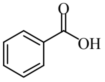
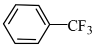
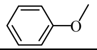


Fig. 6. The influences of the amounts of catalyst (a) and ascorbic acid (b), acetic acid concentration (c), and reaction time (d) on phenol yields in the hydroxylation of benzene. Reaction conditions: benzene (5 mmol), catalyst (0.11 mmol metal), solvent (5 mL), O_2 (1.5 MPa), 105 °C.

Table 2
Hydroxylation of arenes to phenols with O_2 catalyzed by V@CN.



Entry	Substrate	Yield (%)	Selectivity (%)		
			o-	*m-*	*p-*
1		12.2	43	0	57
2		15.5	36	0	64
3		7.7	39	0	61
4		6.5	38	30	32
5		6.2	47	22	31
6		10.7	45	26	29
7		9.9	41	26	32
8		4.0	27	45	23
9		—	—	—	—

Reaction conditions: substrate (10 mmol), catalyst (100 mg, 0.11 mmol V), ascorbic acid (1.5 mmol), O_2 (1.5 MPa), water (5 mL), acetic acid (5 mL), 105 °C, 11 h.

corresponding phenols in moderate yields (Table 2, entries 4–7). But the isomeric distributions in these reactions (*o*-, *m*-, and *p*-) were irregular. Interestingly, no reaction was observed for the hydroxylation of anisole under the same reaction conditions (Table 2, entry 9).

3.4. Catalyst reusability

During the reaction, the catalyst V@CN was practically insoluble in the reaction system, and the heterogeneous catalysts can be recovered conveniently by centrifugation after each reaction run. The reusability of V@CN was tested and the results are shown in Fig. 7. No significant loss of conversion and selectivity was observed after four runs, which shows that V@CN can be reused at least four times. To test if the vanadium species was leaching into solution, we measured the vanadium content of the catalyst after the 4th reaction by ICP-AES, and about 15% of the vanadium was lost after four reaction cycles.

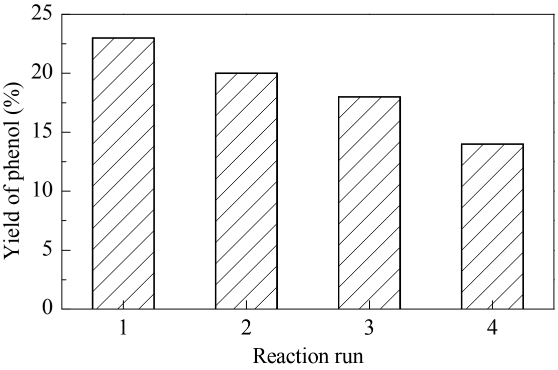
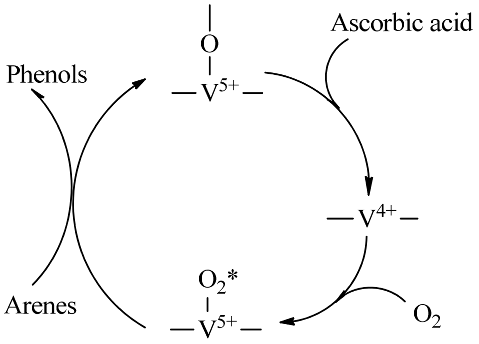


Fig. 7. Catalytic reusability of V@CN in the hydroxylation of benzene to phenol. Reaction conditions: benzene (5 mmol), catalyst (100 mg, 0.11 mmol V), ascorbic acid (1.5 mmol), H_2O (5 mL), acetic acid (5 mL), 105 °C, 11 h.



Scheme 1. The proposed reaction mechanism.

3.5. Catalysis mechanism

To obtain some insights into the reaction mechanism, some control experiments were performed. First, a stoichiometric reaction of V@CN (containing 0.11 mmol) and benzene (5 mmol) with O_2 (1.5 MPa) in the absence of ascorbic acid gave trace amounts of phenol. But pre-treating the V@CN (0.11 mmol V^{4+}) with ascorbic acid (3 mmol) gave 0.05 mmol of phenol under similar reaction conditions, which implied that the V^{4+} species are the active centers (1 mmol benzene; 1.5 MPa O_2; in the absence of ascorbic acid). Based on these results, the hydroxylation mechanism in Scheme 1 has been proposed. The V^{4+} species are oxidized by O_2 to generate an activate peroxide intermediate species V^{5+}–O_2. This vanadium peroxide then attacks the substrates to produce the corresponding phenols and release a V^{5+} species. Finally, this V^{5+} species is reduced to V^{4+} by ascorbic acid and the catalytic cycle is complete. The XPS and ESR spectra showed that the V@CN catalyst contained both V^{4+} and V^{5+} species (in both fresh and recycled V@CN), which implied that the catalyst was ready for hydroxylation, and this is in agreement with the proposed mechanism. Moreover, V^{5+}–O_2 in V@CN should be more reactive towards arenes with electron-withdrawing substituted groups, and the corresponding phenols can be obtained. No phenols can be obtained with arenes with electron-donating substituted groups. The V^{5+}–O_2 species in V@CN catalyst coordinated to N and O are different from the V_xO_y species coordinated to O, thus giving V@CN its activity and selectivity.

4. Conclusions

The vanadium doped carbon nitride catalyst (V@CN) was designed and prepared and shown to be active for the direct hydroxylation of arenes to phenols with O_2. Functional arenes with electron-withdrawing groups such as CN, NO_2, COOH, CF_3, and $COCH_3$ were oxygenated into the corresponding phenols in moderate yields. The catalyst was also applicable for the hydroxylation of aromatic halides (F, Cl, and Br). This catalyst showed the potential for vanadium in the activation of C–H bonds in functionalized arenes with electron-withdrawing groups.

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Graphical Abstract

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Direct hydroxylation of arenes with O_2 catalyzed by V@CN catalyst

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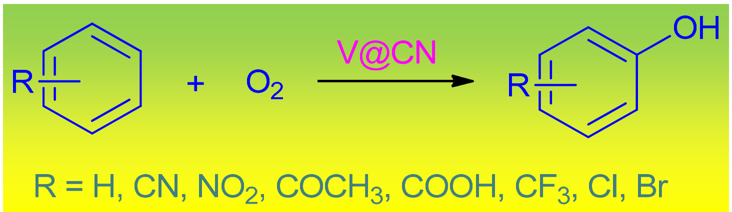

Benzenes with electron-withdrawing groups were oxygenated to the corresponding phenols in considerable yields, and the V@CN catalyst was also applicable for the hydroxylation of aromatic halides (F, Cl, and Br) with O_2.

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