A series of Ce$_x$-V-g-C$_3$N$_4$ catalysts with different cerium content were synthesized by a facile co-assembly method. Compared with pure V-g-C$_3$N$_4$ catalyst, the addition of cerium facilitated the high dispersion of vanadium species as well as the benzene adsorption ability of the corresponding catalysts. Also, the existence of cerium promoted the partial reduction of vanadium species, which improved the redox property of vanadium species as the active centres. The Ce$_{0.07}$-V-g-C$_3$N$_4$ catalysts showed considerably improved activity in the benzene hydroxylation reaction compared with V-g-C$_3$N$_4$ catalyst. Among the catalysts studied, Ce$_{0.07}$-0.07 V-g-C$_3$N$_4$ exhibited the best catalytic activity with a benzene conversion of 33.7% and a phenol yield of 32.3% with good structural and catalytic stability, while only 24.7% of benzene conversion and phenol yield of 24.2% were obtained over 0.07 V-g-C$_3$N$_4$.

1. Introduction

Phenol, as an important chemical intermediate in industry, is widely employed in the synthesis of aniline, resins, plastics, bactericides and agrochemicals [1]. However, the current phenol production is based upon the three-step cumene process, which has some inevitable disadvantages, e.g. the by-product acetone with low market demand, the complex synthesis steps and the high energy consumption [2]. From the view of green chemistry, the direct hydroxylation of benzene to phenol has attracted great interest in the past few decades.
Since it is difficult to insert an oxygen atom into the stable C–H bond of benzene, many efforts have been devoted to searching for appropriate oxidants [3]. Among them, molecular oxygen, nitrous oxide and hydrogen peroxide are three main kinds of oxidants used in the benzene hydroxylation reaction [4–7]. However, molecular oxygen is too stable to be activated mildly, while nitrous oxide is not easily available in industry. In contrast, hydrogen peroxide shows superior properties with the mild reaction condition of benzene oxidation and water as the green by-product.

Up to now, catalysts with various metal species, such as V, Fe, Cu, Co and Ti [8–12], have been employed for this titled reaction. Among them, vanadium species exhibit excellent catalytic activity. As for the catalyst support, many metal oxides such as Al2O3, SiO2 and TiO2 were widely used [13–15]. However, the weak interaction between V species and the metal oxide support leads to undesirable loss of V active spices [16]. Besides, some metal oxide supports, such as Al2O3 and ZrO2, disfavour the redox cycle between V5+ and V4+ [17,18], leading to the low activity in the direct oxidation of benzene to phenol.

Nowadays, graphitic carbon nitride (g-C3N4), as an analogue of graphene, has been widely used as a catalyst support, due to its unique physico-chemical property and easily modified feature. Compared with pure graphene, the N-containing groups with strong coordination ability may facilitate the dispersion and stability of metal species. Moreover, carbon support will show certain reduction ability at high temperature, affecting the valence state of loaded metal species [19–21]. In previous work [22], we found that V5+ species were partially reduced to V4+ ones during the calcination process over g-C3N4 support. And the resulting V-g-C3N4 catalyst showed excellent catalytic performance and stability in the direct benzene hydroxylation. As is known, the transformation between V5+ and V4+ species plays an important role in the benzene conversion. Therefore, it is worth exploring the proper molar ratio of V4+/V5+ to obtain the most effective catalyst for the titled reaction.

Recently, bi-metal or multi-metal catalysts have shown competitive advantages in redox reactions. As the most abundant rare earth element, cerium is widely used in catalytic oxidation due to its unique electronic structures. The different electronic configurations between Ce3+ with 4f15d0 and Ce4+ with 4f05d0 lead to the formation of good redox couple of Ce3+/Ce4+ [23]. Paz et al. found that the addition of second metal cerium enhanced the interactions between Pt0 and oxygen atoms. As a result, the bi-metal catalyst showed higher activity in the CO oxidation reaction even at lower reaction temperature compared with the non-promoted Pt catalysts [24]. Lu et al. prepared a series of CeO2–Co3O4 catalysts for the catalytic oxidation of formaldehyde (HCHO) [25]. The unique redox property of Ce played a crucial role in the excellent performance in HCHO oxidation.

In this study, we added cerium as the second metal into V supported g-C3N4 in order to facilitate the redox property of V species. A series of cerium-doped V-g-C3N4 catalysts were prepared by a facile co-assembly method using vanadylacetylacetonate, cerium nitrate and melamine as precursors. All the Ce doped V-g-C3N4 catalysts showed higher activity than the mono-metal ones. The strong synergistic effects between Ce and V result in the excellent redox property of V species, which improves the catalytic performance of corresponding catalysts in benzene hydroxylation.

2. Material and methods

2.1. Synthesis

Melamine, vanadylacetylacetonate (C10H14O5V) and Ce(NO3)3·6H2O were all purchased from Aladdin Industrial Corporation and used without further purification. g-C3N4 was prepared by the direct calcination of melamine at 550°C for 2 h under nitrogen atmosphere [26]. 0.07 V-g-C3N4 sample was obtained as follows: 0.42 g of C10H14O5V and 2.50 g of melamine were mixed with 50 ml of ethanol. After stirring vigorously at 50°C for 1 h, the solution was dried at 60°C overnight. The resulting solid sample was calcined in N2 from room temperature to 550°C with a heating rate of 2°C min−1 and kept at 550°C for another 2 h. After cooling to room temperature, the product was collected and denoted as 0.07 V-g-C3N4, where 0.07 represented the theoretical weight content of vanadium. 0.05 V-g-C3N4 and 0.10 V-g-C3N4 catalysts were prepared according to the same synthesis procedure as for 0.07 V-g-C3N4 by adding desired amount of C10H14O5V.

As for 0.07Ce-g-C3N4, the synthesis method was also similar to that of 0.07 V-g-C3N4, except for adding 0.23 g of Ce(NO3)3·6H2O rather than 0.42 g of C10H14O5V. Furthermore, by adding both 0.42 g of C10H14O5V and different amounts of Ce(NO3)3·6H2O, Ce–0.07 V-g-C3N4 catalysts were obtained, where x represents the molar ratio of Ce/V.
2.2. Benzene hydroxylation reaction

The direct benzene hydroxylation reaction was conducted as follows. Typically, 1 ml of benzene, 10 ml of 80 wt% acetic acid and 40 mg of catalyst were added into a 25 ml three-necked flask connected with a reflux condenser. After heating to 70°C, 3.5 ml of 30 wt% H₂O₂ was added dropwise in 30 min with vigorously stirring. The reaction mixture was stirred for another 4 h. After reaction, the catalyst was separated by centrifugation and the content of liquid products was analysed immediately by gas chromatography using toluene as the internal standard.

2.3. Material characterization

Elemental analysis was performed with a Thermo Elemental IRIS Intrepid inductively coupled plasma-atomic emission spectrometer (ICP-AES). Transmission electron microscopic (TEM) images were acquired with a FEI Tecnai G² F20 S-Twin field-emission transmission electron microscope operated at 200 kV. Elemental mapping was conducted using a Philips XL 30 microscope with energy dispersive X-ray spectrometer operated at 30 kV. Fourier transform infrared (FT-IR) spectra were recorded with a Nicolet iS10 infrared instrument using KBr discs. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advances X-ray diffractometer using Cu-Kα radiation with a voltage of 40 kV and a current of 40 mA. X-ray photoelectron spectra (XPS) were recorded with a Perkin-Elmer PHI 5000C ESCA system equipped with a dual X-ray source by using Mg Kα (1253.6 eV) anode and a hemispherical energy analyser. Fourier transform infrared (FT-IR) spectra were recorded with a Nicolet iS10 infrared instrument using KBr discs. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advances X-ray diffractometer using Cu-Kα radiation with a voltage of 40 kV and a current of 40 mA. X-ray photoelectron spectra (XPS) were recorded with a Perkin-Elmer PHI 5000C ESCA system equipped with a dual X-ray source by using Mg Kα (1253.6 eV) anode and a hemispherical energy analyser. Specific surface area results were obtained at 77 K using a Micromeritics Tristar 3000 apparatus. The benzene adsorption was measured using a Hiden intelligent gravimetric analyser. All samples were degassed under a vacuum of less than 10⁻³ Pa at 300°C for 6 h prior to the adsorption measurement.

3. Results and discussion

The results of benzene hydroxylation reaction over all catalysts studied are shown in table 1 and electronic supplementary material, table S1. By optimizing the vanadium content in the catalysts, the best catalytic activity in the benzene hydroxylation reaction was obtained over 0.07 V-g-C₃N₄ catalyst with 7 wt% of vanadium content. With the introduction of cerium into the 0.07 V-g-C₃N₄ catalyst (Ce/V = 0.05), the benzene conversion is improved slightly from 24.7% to 25.3% (entry 2, table 1). With the further rise of cerium content, the benzene conversion increases remarkably to the highest 33.7% over Ce₀.₀₇-₀.₀₇ V-g-C₃N₄ (entry 3, table 1) and then decreases to 29.4% over Ce₀.₁₀-₀.₀₇ V-g-C₃N₄ (entry 4, table 1), while the phenol selectivity remains almost constant with the variation of cerium content. Moreover, the carbon balance value shown in table 1 are greater than 99% over the three Ce-containing catalysts, indicating a high carbon yield with negligible side reactions. The TOF value of 17.1 h⁻¹ based on the vanadium content also indicates that Ce₀.₀₇-₀.₀₇ V-g-C₃N₄ is the most active catalyst. Thus, we deduce that a proper molar ratio of Ce/V possibly facilitates both the redox properties of V species and the efficient decomposition of H₂O₂, leading to the remarkable catalytic activity in the benzene conversion reaction [27].

In order to elucidate the synergistic effects between V and Ce species, we selected g-C₃N₄, 0.07 V-g-C₃N₄ and Ce₀.₀₇-₀.₀₇ V-g-C₃N₄ as the representative catalysts to carry out detailed characterizations. Generally, the specific surface area of a catalyst has a certain influence on the catalytic activity. As shown in table 2, the specific surface area increases slightly after the introduction of metal species compared with that of the non-modified g-C₃N₄ catalyst (entries 1–3) and Ce₀.₀₇-₀.₀₇ V-g-C₃N₄ has the highest specific surface area. However, the quite different catalytic performances between 0.07 V-g-C₃N₄ and Ce₀.₀₇-₀.₀₇ V-g-C₃N₄ demonstrate that the specific surface area is not the main reason for the different catalytic activity.

The morphologies of the catalysts were studied by TEM. As shown in figure 1a–d, all the samples exhibit the typical large lamellar structure, indicating that the structure of g-C₃N₄ support remains after the incorporation of metal species. As for 0.07 V-g-C₃N₄ and Ce₀.₀₇-₀.₀₇ V-g-C₃N₄ catalysts (figure 1b–d), no obvious metal particles are observed over both catalysts, implying the high dispersion of metal species. Also, the element-mapping images of 0.07 V-g-C₃N₄ and Ce₀.₀₇-₀.₀₇ V-g-C₃N₄ catalysts (figure 1e–g) further demonstrate that both V and Ce species are highly dispersed over the g-C₃N₄ support.

However, it is worth noting that the vanadium dispersion of 0.07 V-g-C₃N₄ is slightly poorer than that of Ce₀.₀₇-₀.₀₇ V-g-C₃N₄. This implies that the existence of cerium may facilitate the high dispersion of vanadium, leading to the high catalytic activity [28].
Table 1. Catalytic activity of various catalysts for benzene hydroxylation reaction. Reaction conditions: 1 ml of benzene, 10 ml of 80 wt% acetic acid, 40 mg of catalyst, 3.5 ml of 30 wt% H$_2$O$_2$, 70°C for 4 h.

| entry | catalyst       | benzene conv. (%) | phenol select. (%) | phenol yield (%) | TOFa value (h$^{-1}$) | carbon in (mmol) | unreacted benzene (mmol) | phenol (mmol) | by-productsb (mmol) | carbon balance closurec (%) |
|-------|----------------|-------------------|--------------------|------------------|-----------------------|------------------|---------------------------|----------------|-------------------|---------------------------|
| 1     | 0.07 V-g-C$_3$N$_4$ | 24.7              | 98.1               | 24.2             | 12.4                  | 67.6             | 50.9                      | 16.4           | 0.2               | > 99                      |
| 2     | Ce$_{0.05}$-0.07 V-g-C$_3$N$_4$ | 25.3              | 96.3               | 24.4             | 12.7                  | 67.6             | 50.5                      | 16.5           | 0.5               | > 99                      |
| 3     | Ce$_{0.07}$-0.07 V-g-C$_3$N$_4$ | 33.7              | 95.9               | 32.3             | 17.1                  | 67.6             | 44.8                      | 21.8           | 0.9               | > 99                      |
| 4     | Ce$_{0.10}$-0.07 V-g-C$_3$N$_4$ | 29.4              | 97.6               | 28.7             | 15.1                  | 67.6             | 47.7                      | 19.4           | 0.5               | > 99                      |

*Turnover frequency (TOF) was calculated as the molecules of generated phenol per metal atom per hour.

bThe total amount of hydroquinone and catechol.

cThe carbon balance closure was calculated as the molar ratio of carbon out to carbon in.
Figure 1. TEM images of (a) g-C₃N₄, (b) 0.07 V-g-C₃N₄ and (c,d) Ce₀.₀⁰₇-0.₀⁰₇ V-g-C₃N₄. V mapping of (e) 0.07 V-g-C₃N₄ and (f) Ce₀.₀⁰₇-0.₀⁰₇ V-g-C₃N₄ and Ce mapping of (g) Ce₀.₀⁰₇-0.₀⁰₇ V-g-C₃N₄.

Table 2. Specific surface area and metal contents of various catalysts.

| entry | catalyst                | S_BET (m² g⁻¹) | vanadium content (wt.%)<sup>a</sup> | cerium content (wt.%)<sup>a</sup> |
|-------|-------------------------|----------------|------------------------------------|----------------------------------|
| 1     | g-C₃N₄                 | 32             | —                                  | —                                |
| 2     | 0.07 V-g-C₃N₄          | 43             | 7.0                                | —                                |
| 3     | Ce₀.₀⁰₇-0.₀⁰₇ V-g-C₃N₄ | 47             | 6.8                                | 0.5                              |

<sup>a</sup>Analysed by ICP-AES.

The graphitic stacking structures of the catalysts were also confirmed by XRD patterns. For pure g-C₃N₄ (electronic supplementary material, figure S1a), two distinct diffractions are observed at ca 13.2° and 27.5°, corresponding to (100) diffraction of in-planar repeating motifs of tris-s-triazine units and (002) diffraction of interlayer stacking aromatic systems, respectively [29]. After the addition of metal species, both corresponding (100) and (002) diffraction peaks become broader, suggesting that the ordered structure of g-C₃N₄ support decreases slightly. In addition, the (002) peaks of 0.07 V-g-C₃N₄ and Ce₀.₀⁰₇-0.₀⁰₇ V-g-C₃N₄ catalysts both shift to low angle slightly compared with that of g-C₃N₄, indicating that the metal oxides were incorporated into the g-C₃N₄ sheets successfully [30]. Furthermore, no distinct peak originating from either vanadium or cerium species can be observed, which implies that the metal species are in non-crystallized state or dispersed well on the g-C₃N₄ layers. These results are consistent with the results of TEM.
The FT-IR spectra of g-C3N4, 0.07 V-g-C3N4 and Ce0.07-0.07 V-g-C3N4 catalysts are shown in figure 2. As for g-C3N4 (figure 2a), the major bands between 1200 and 1650 cm⁻¹ are attributed to the stretching modes of CN heterocycles, while the band at 804 cm⁻¹ corresponds to the stretching mode of triazine units (C₆N₇). The broad bands in the range of 3000–3400 cm⁻¹ can be ascribed to the stretching of N–H bonds in both uncondensed amino groups and adsorbed water molecules [31]. For 0.07 V-g-C3N4 and Ce0.07-0.07 V-g-C3N4 (figure 2b,c), their spectra are similar to that of g-C3N4 except for a small additional band at 2157 cm⁻¹ corresponding to the disturbance of conjugated N=C=N units after metal doping [32,33].

In order to investigate the surface chemical composition of the catalysts, XPS measurement was carried out. As shown in electronic supplementary material, figure S2, C and N species, which refer to the peaks at binding energies of 288.0 (C 1s) and 400.0 (N 1s), are the main elements in all catalysts. By subtracting the peak area of the contaminant carbon C 1s at 284.6 eV, the peak area ratios of C 1s/N 1s of g-C3N4, 0.07 V-g-C3N4 and Ce0.07-0.07 V-g-C3N4 catalysts are 0.89, 0.83 and 0.73, respectively. As the theoretical molar ratio of C/N in g-C3N4 is 3/4, the correction factor between peak area ratio of C/N and molar ratio of C/N should be 1.187. Based on the correction factor, the C/N molar ratio of 0.07 V-g-C3N4 and Ce0.07-0.07 V-g-C3N4 can be calculated as 3/4.3 and 3/4.9, respectively, which implies the formation of N-rich carbon nitride by the incorporation of metal species. The reason for
Table 3. The ratios of V species with different valence states on the catalyst surface.

| entry | catalyst                          | \( V^{4+}/V^{3+} \) | \( (V^{4+}+V^{3+})/V^{2+} \) | \( V^{3+}/V^{2+} \) |
|-------|----------------------------------|---------------------|-------------------------------|---------------------|
| 1     | 0.07 V-g-C\(_3\)N\(_4\)         | 0.45                | 0.45                          | —                   |
| 2     | Ce\(_{0.05}\)-0.07 V-g-C\(_3\)N\(_4\) | 0.53                | 0.93                          | 0.78                |
| 3     | Ce\(_{0.07}\)-0.07 V-g-C\(_3\)N\(_4\) | 0.62                | 1.09                          | 0.75                |
| 4     | Ce\(_{0.25}\)-0.07 V-g-C\(_3\)N\(_4\) | 0.64                | 1.15                          | 0.74                |
| 5     | 0.07 V-g-C\(_3\)N\(_4\) recycled | 0.48                | 0.48                          | —                   |
| 6     | Ce\(_{0.07}\)-0.07 V-g-C\(_3\)N\(_4\) recycled | 0.49                | 0.85                          | 0.73                |

the C/N molar ratio variation may be caused by the increase of \(-\text{NH}\) groups on the g-C\(_3\)N\(_4\) support surface as the metal species destroy the ordered structure of g-C\(_3\)N\(_4\) partially. As reported previously, in preparation of C–N materials, the addition of metal species restrained the decomposition of nitrogen species and accelerated the decomposition of carbon species, leading to high N content in the samples [34,35]. As shown in figure S5, the C 1s spectrum of g-C\(_3\)N\(_4\) can be deconvoluted into three peaks with binding energies of 284.6, 285.7 and 287.5 eV, corresponding to the graphitic carbon (C–C), C–O and sp\(^2\) hybridized carbon (N–C=N), respectively [36]. After the incorporation of metal species, the peak intensities of both C–O and N–C=N increase, while that of C–C decreases. These imply that the rigid structural regularity of g-C\(_3\)N\(_4\) was partially broken and more defects were produced on the surface of g-C\(_3\)N\(_4\), generating more sites for metal species anchoring. In figure S6, the N 1s spectrum of g-C\(_3\)N\(_4\) shows three main peaks at 398.2, 399.3 and 400.6 eV, assigned to triazine nitrogen (C=N–C), tertiary nitrogen (N=–(C)) and amino function group (N–H), respectively [37]. It is worth noting that both the C 1s and N 1s peak positions of 0.07 V-g-C\(_3\)N\(_4\) and Ce\(_{0.07}\)-0.07 V-g-C\(_3\)N\(_4\) are slightly shifted to high binding energy regions compared with those of g-C\(_3\)N\(_4\). Since the graphite analogue CN matrix is believed to stabilize the metal species with the ‘coordination nest’ consisting of C and N atoms [38], it is reasonable to deduce that a strong interaction between metal species and g-C\(_3\)N\(_4\) support may exist, which is reflected in the XPS study. In addition, as shown in the V 2p\(_{3/2}\) XPS spectra (figure 4), 0.07 V-g-C\(_3\)N\(_4\) merely contains V\(^{5+}\) and V\(^{4+}\), while V\(^{3+}\) species appear in Ce\(_{0.07}\)-0.07 V-g-C\(_3\)N\(_4\). Also, the content of low oxidation state V (V\(^{4+}\), V\(^{3+}\)) species increases after the addition of cerium (figure 4b–d). These may be ascribed to the reduction of partial V\(^{5+}\) species by the Ce\(^{3+}\) species during calcination [39]. In fact, similar results were reported for other Ce–V catalysts [40,41]. As listed in table 3, the (V\(^{4+}\)+V\(^{3+}\))/V\(^{2+}\) ratio (calculated by the corresponding area ratio) increases gradually from 0.45 to 1.15 with the increase of cerium content, corresponding to the rise of low oxidation state vanadium species. It seems that Ce\(^{3+}\)/Ce\(^{4+}\) species play an important role in maintaining the content of V\(^{4+}\) and V\(^{3+}\) species. During the oxidation of benzene to phenol over vanadium-containing catalyst using H\(_2\)O\(_2\) as an oxidant, the low valent vanadium species can be oxidized to V\(^{5+}\)–O• or V\(^{4+}\)–O• radicals which perform as main active centres for the conversion of benzene to phenol [42]. In electronic supplementary material, figure S5, the V 2p\(_{3/2}\) XPS measurements of both 0.07 V-g-C\(_3\)N\(_4\) and Ce\(_{0.07}\)-0.07 V-g-C\(_3\)N\(_4\) catalysts were conducted after four recycles. The recovered Ce\(_{0.07}\)-0.07 V-g-C\(_3\)N\(_4\) catalyst shows little change in the ratios of (V\(^{4+}\)+V\(^{3+}\))/V\(^{5+}\) and V\(^{3+}\)/V\(^{4+}\) relative to the fresh one, indicating that the excellent redox ability of Ce\(^{3+}\)/Ce\(^{4+}\) improves the redox cycles of V\(^{5+}\)/V\(^{4+}\) and V\(^{4+}\)/V\(^{3+}\). Comparing with Ce\(_{0.07}\)-0.07 V-g-C\(_3\)N\(_4\), the recovered Ce\(_{0.07}\)-0.07 V-g-C\(_3\)N\(_4\) catalyst has small amount of Ce\(^{4+}\) species with the appearance of Ce\(^{4+}\) fingerprint (electronic supplementary material, figure S6) [43]. The existence of Ce\(^{3+}\)/Ce\(^{4+}\) is confirmed, which promotes the formation of low state vanadium. However, •OH radicals produced by V\(^{4+}\) lead to overoxidation of benzene [44]. It is believed that V\(^{4+}\) species are more reactive than V\(^{5+}\) ones during the benzene conversion [45]. Thus a proper molar ratio of (V\(^{4+}\)+V\(^{3+}\))/V\(^{5+}\) may be beneficial to achieve a good conversion of benzene and a high selectivity of phenol. Therefore, in the present case, it is reasonable to indicate that the addition of proper cerium amount improves the redox capacity of active vanadium species along with the efficient decomposition of hydrogen peroxide.

The adsorption properties of g-C\(_3\)N\(_4\), 0.07 V-g-C\(_3\)N\(_4\) and Ce\(_{0.07}\)-0.07 V-g-C\(_3\)N\(_4\) catalysts were evaluated by studying the gravimetric uptake of benzene. In figure 5a, pure g-C\(_3\)N\(_4\) exhibits an evident adsorption of benzene, probably attributed to the strong π–π interactions between benzene molecules and g-C\(_3\)N\(_4\) [28]. Interestingly, Ce\(_{0.07}\)-0.07 V-g-C\(_3\)N\(_4\) exhibits the highest benzene adsorption ability among all the catalysts. As reported earlier [46,47], by increasing the content of surface basic groups...
Figure 4. V 2p₃/₂ XPS spectra of (a) 0.07 V-g-C₃N₄, (b) Ce₀.₇₋₅₋₀.₀₇ V-g-C₃N₄, (c) Ce₀.₀₇₋₁₋₀.₀₇ V-g-C₃N₄ and (d) Ce₀.₁₀₋₀.₀₇ V-g-C₃N₄.

Figure 5. (a) The benzene adsorption isotherms of (a) g-C₃N₄, (b) 0.07 V-g-C₃N₄, (c) Ce₀.₀₇₋₀.₀₇ V-g-C₃N₄ at 298 K. (b) Cyclic utilization of Ce₀.₀₇₋₀.₀₇ V-g-C₃N₄.

(e.g. amino or hydroxyl groups) in activated carbon, the adsorption affinity for the nonpolar molecules, e.g. benzene, was enhanced. Therefore, combining with the results of XPS, it is reasonable to deduce that the increase of nitrogen-containing groups in g-C₃N₄ support after doping metal species can promote the benzene adsorption ability of the corresponding catalyst effectively, leading to the excellent benzene conversion.

The reusability of Ce₀.₀₇₋₀.₀₇ V-g-C₃N₄ catalyst was investigated as it showed the best catalytic activity in the target reaction (figure 5b). After each reaction, the Ce₀.₀₇₋₀.₀₇ V-g-C₃N₄ catalyst was separated, washed and dried for the next fresh reaction. After four recycles, the catalyst retained high activity without marked loss in both benzene conversion and phenol selectivity. The vanadium content of both the last recycled catalyst and the reaction solution was measured by ICP-AES, and no leaching of vanadium happened (entry 9, electronic supplementary material, table S1). In table 3, as expected, the (V⁴⁺ + V³⁺)/V⁵⁺ peak area ratio of recovered Ce₀.₀₇₋₀.₀₇ V-g-C₃N₄ is 0.85, much higher than that of recovered 0.07 V-g-C₃N₄. These further demonstrate that the existence of Ce species facilitates the formation of V⁴⁺ and V³⁺ species. Moreover, XRD and FT-IR (electronic supplementary material, figures S3 and S4) measurements were conducted for the recovered Ce₀.₀₇₋₀.₀₇ V-g-C₃N₄ from the fourth run.
The structural properties of the recovered catalyst are nearly identical to those of fresh one, indicating the strong interactions between metal species and g-C3N4 support which accounts for high stability of Ce0.07−0.07 V-g-C3N4 in the direct benzene hydroxylation. The excellent stability is because of abundant defects of g-C3N4 after cerium modification that improve the dispersion and stability of V species. Although the role of Vδ+ species remains to be further studied, the work gives an insight into the design of efficient catalysts for the titled reaction in future.

A possible reaction mechanism of benzene hydroxylation is proposed based on literature work [22]. Benzene is chemically adsorbed onto the surface of g-C3N4, and then the surface dispersed Vδ+ species are oxidized by H2O2 to produce Vδ+\(\cdot\)O\(\cdot\) radicals and H2O. The main active Vδ+\(\cdot\)O\(\cdot\) radicals are rapidly activated and react with adsorbed benzene to gain the target phenol and Vδ+ is reduced to Vδ++. At the same stage, the redox Vδ+\(\cdot\)Vδ+ is supported by Ceδ+/Ceδ++ to accelerate the reaction into the next recycle.

4. Conclusion

In this work, we developed a facile method to synthesize cerium-doped V-g-C3N4 catalysts for the direct oxidation of benzene to phenol. The dispersion of vanadium species was distinctly improved after the addition of cerium species. Among the catalysts studied, Ce0.07−0.07 V-g-C3N4 showed excellent catalytic performance with good reusability in the titled reaction, ascribed to the enhanced vanadium redox property, improved benzene adsorption ability and strong interactions between metal species and g-C3N4 support.

Data accessibility. The datasets supporting this article have been uploaded as part of the electronic supplementary material.

Authors’ contributions. C.W., L.H. and M.W. performed the experiments and collected data. B.Y. and H.H. designed and directed the study and also wrote the manuscript. All authors gave final approval for publication.

Competing interests. The authors declare that they have no competing interests.

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