Highly Dispersed Vanadia Anchored on Protonated g-C₃N₄ as an Efficient and Selective Catalyst for the Hydroxylation of Benzene into Phenol

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Abstract: The direct hydroxylation of benzene is a green and economical-efficient alternative to the existing cumene process for phenol production. However, the undesired phenol selectivity at high benzene conversion hinders its wide application. Here, we develop a one-pot synthesis of protonated g-C₃N₄ supporting vanadia catalysts (V-pg-C₃N₄) for the efficient and selective hydroxylation of benzene. Characterizations suggest that protonating g-C₃N₄ in diluted HCl can boost the generation of amino groups (NH/NH₂) without changing the bulk structure. The content of surface amino groups, which determines the dispersion of vanadia, can be easily regulated by the amount of HCl added in the preparation. Increasing the content of surface amino groups benefits the dispersion of vanadia, which eventually leads to improved H₂O₂ activation and benzene hydroxylation. The optimal catalyst, V-pg-C₃N₄-0.46, achieves 60% benzene conversion and 99.7% phenol selectivity at 60 °C with H₂O₂ as the oxidant.

Keywords: benzene hydroxylation; vanadia; g-C₃N₄; phenol; protonation

1. Introduction

Phenol, one of the most valuable organic intermediates for fine chemical manufacturing [1,2], is produced industrially by a three-step cumene process from benzene [3]. Unfortunately, this process suffers from high energy consumption, relatively low yield, and large amount of acetone as by-products [4,5]. To address these problems, extensive efforts have been devoted to developing an economical efficient and green approach for phenol production. Among various methods, the direct hydroxylation of benzene to phenol using H₂O₂ as an oxidant has been recognized as a promising alternative as it can be operated under mild conditions and only produces water as a co-product [4,6]. However, because phenol is more reactive to oxidation than benzene, obtaining high selectivity to phenol at high benzene conversion is difficult [7,8]. To this end, a key topic for the catalytic hydroxylation of benzene is the development of advanced catalysts to achieve high activity and benzene selectivity simultaneously.

Recently, graphitic carbon nitride (g-C₃N₄) has emerged as a fascinating material to load active metals for benzene hydroxylation [9–12]. As an analog of graphite, g-C₃N₄ possesses a stacked 2D structure with π-conjugated planar layers, which endow it with high capability in activating aromatic molecules (e.g., benzene) [13]. Meanwhile, the rich uncondensed aliphatic amines, in the form of –NH₂ and –NH– groups, provide abundant anchor sites for active species [14–16]. Because the planar adsorption of benzene on the surface of g-C₃N₄ is stronger than the non-planer adsorption of phenol [17], g-C₃N₄-supported catalysts usually exhibit good phenol selectivity in benzene hydroxylation, regardless of the supported transition metals (Cu, Fe, V, Co, Ni). The key problem for g-C₃N₄-based catalysts then becomes “how to improve the benzene conversion”. A frequently
used strategy is to optimize the type and loading amount of metal sites. For example, Ding et al. [4] synthesized a series of metal-doped g-C₃N₄ catalysts and found that V-g-C₃N₄ was the most efficient one. Under optimal conditions, V-g-C₃N₄ can achieve 18.2% benzene conversion and 100% phenol selectivity. Wang et al. [18] optimized the loading of vanadia and found that 8V/g-C₃N₄ exhibited superior activity with a benzene conversion of 24.6% and phenol selectivity of 99.2%. Recently, Wang et al. [8] doped cerium into V/g-C₃N₄ catalysts by a simple co-assembly strategy and found that Ce₀.₀⁷/0.₀⁷V/g-C₃N₄ greatly improved catalytic activity with 33.7% benzene conversion and 95.9% phenol selectivity.

At a fixed loading amount of vanadium, the structure of g-C₃N₄ also affects the catalytic performance of V-g-C₃N₄. For example, using mesoporous carbon nitride as a support material can increase the surface area of g-C₃N₄ and the dispersion of vanadia to improve the benzene conversion [19,20]. Recently, Xu et al. reported that exfoliated and protonated g-C₃N₄ can provide more anchor sites for the immobilization of active species [21]. They proposed that the chemical environment (especially its nitrogen species) of g-C₃N₄ is critical to the loading of vanadia. Notably, the protonation of g-C₃N₄ was usually conducted in strong acidic conditions, which not only change the local chemical environment but also the surface area. To investigate the intrinsic influence of the chemical environment of g-C₃N₄ on the vanadia dispersion and the catalytic performance, a synthetic method that can regulate the surface structure of g-C₃N₄ without changing the bulk structures is highly desired.

Herein, we develop a one-pot synthesis of V-pg-C₃N₄ to regulate the surface amino groups of g-C₃N₄ without changing the bulk structure and surface area. Characterizations and catalytic tests suggest that the content of surface amino groups is a decisive factor for the dispersion of vanadia and can quasi-linearly influence the catalytic performance of V-pg-C₃N₄ in the direct hydroxylation of benzene to phenol. A maximum of 60% benzene conversion and 99.7% selectivity to phenol can be achieved at 60 °C on V-pg-C₃N₄-0.46, which is attributed to the high dispersion of V species stabilized by amino groups, the presence of V⁴⁺/V⁵⁺ redox pairs, and the cooperative benzene-activation capability of g-C₃N₄. The mass specific activity of V-pg-C₃N₄-0.46 is as high as 4.26 and 2.11 g g⁻¹ h⁻¹, which exceeds most reported results (Table 1).

**Table 1.** The catalytic activity of various vanadia- and g-C₃N₄-based catalysts for benzene hydroxylation.

| Catalyst                      | V<sub>b</sub> (mL) | V<sub>H₂O₂</sub> (mL) | W<sub>catal</sub> (mg) | T (K) | t (h) | Conv. (%) | Sel. (%) | Specific Activity (h⁻¹) | Ref. |
|-------------------------------|-------------------|-----------------------|-----------------------|-------|-------|-----------|----------|------------------------|-----|
| 0.4V-g-C₃N₄                  | 1.0               | 3                     | 60                    | 333   | 6     | 17.7      | 100      | 0.52                   | [4] |
| H₂PMo₁₀V₂O₄₀/pg-C₃N₄         | 1.0               | 4.1                   | 100                   | 333   | 8     | 25.8      | 99.7     | 0.34                   | [22]|
| VO/MCM-41-NH₂                | 0.9               | 1                     | 100                   | 333   | 1     | 58.6      | 18.5     | 1.03                   | [6] |
| 8V-g-C₃N₄                    | 1.0               | 3.5                   | 40                    | 343   | 4     | 24.6      | 99.2     | 1.61                   | [18]|
| Fe-g-C₃N₄                    | 1                 | 3                     | 50                    | 333   | 2     | 17.5      | 99.0     | 1.84                   | [23]|
| V₂O₅-mp-C₃N₄                 | 1.5               | 3                     | 60                    | 333   | 3     | 18.7      | 95.9     | 1.59                   | [19]|
| VO-peg-C₃N₄                  | 1.0               | 3                     | 75                    | 333   | 4     | 11.7      | 97.9     | 0.40                   | [21]|
| g-C₃N₄ QD/Fe-SBA-15          | 3                 | 6                     | 120                   | 333   | 3     | 41.7      | 98.8     | 3.01                   | [24]|
| VO₂-SBA-16                   | 0.3               | 1.5                   | 10                    | 333   | 4     | 13.8      | 97.5     | 1.06                   | [25]|
| HPMoV/NH₂-SBA-15             | 1.0               | 3.0                   | 100                   | 333   | 6     | 20.0      | 95.0     | 0.33                   | [26]|
| VO₂-TiO₂                     | 2.6               | 6                     | 180                   | 333   | 5     | 26.3      | 90.0     | 0.72                   | [27]|
| PMoV₅/SiO₂                   | 1.0               | 3.0                   | 150                   | 333   | 6     | 21.6      | 100      | 0.25                   | [28]|
| V₂C-600                      | 0.4               | 1.4                   | 20                    | 343   | 3     | 31.8      | 94.9     | 2.12                   | [29]|
| VO₂-GO                       | 1.0               | 3.5                   | 40                    | 338   | 3     | 23.1      | 98.4     | 1.99                   | [30]|
| Ce₀.₀⁷-0.₀⁷ V-g-C₃N₄         | 1.0               | 3.5                   | 40                    | 343   | 4     | 33.7      | 95.9     | 2.13                   | [8] |
| V-pg-C₃N₄-0.46               | 1.0               | 3.0                   | 60                    | 333   | 5     | 62.0      | 97.0     | 2.11                   |     |
| V-pg-C₃N₄-0.46               | 1.0               | 3.0                   | 60                    | 333   | 1     | 25.0      | 97.0     | 4.26                   | p.w.|

* Specific activity is calculated based on the mass of synthesized phenol per gram of whole catalyst per hour.
* b Present work.
2. Results and Discussion
2.1. Bulk Structures and Surface Structures of V-g-C₃N₄ and V-pg-C₃N₄

Unlike traditional methods that protonate g-C₃N₄ before loading vanadia [21], the one-pot synthesis of V-pg-C₃N₄ was conducted in a mixture of HCl, g-C₃N₄, and vanadyl acetylacetonate where the protonation of g-C₃N₄ and the loading of vanadia took place simultaneously. V-g-C₃N₄ was synthesized in the same way as V-pg-C₃N₄-0.46 except that no HCl was added. As shown in Figure 1a, the diffraction patterns of V-g-C₃N₄ and V-pg-C₃N₄-0.46 are very similar to those of g-C₃N₄, suggesting that vanadia loading and protonation treatment exert little influence on the bulk structure of C₃N₄. Characteristic peaks at 27.5° and 13.6° correspond to (002) and (001) planes of graphitic C₃N₄, which are in accordance with the interlayer stacking structure of aromatic systems and the in-plane reflection of the tri-s-triazine motifs, respectively [31]. N₂ sorption measurements show that g-C₃N₄, V-g-C₃N₄, and V-pg-C₃N₄-0.46 have similar surface areas (ca. 11 m² g⁻¹), excluding the exfoliation of bulk g-C₃N₄ during the protonation treatment in the one-pot synthesis. No distinct peaks related to vanadia-containing phases are observed in V-g-C₃N₄ and V-pg-C₃N₄-0.46, likely due to the low mass loading and high dispersion of vanadia species [32].

![X-ray diffraction (XRD) patterns and Fourier transform infrared spectroscopy (FT-IR) spectra of as-synthesized samples.](image)

Consistent with the similar bulk structure, the samples exhibit very similar FT-IR spectra (Figure 1b). The broad bands at ~3156 cm⁻¹ can be ascribed to the stretching vibration of uncondensed amino functional groups (such as -NH- and -NH₂) on the graphitic sheets and the O-H groups of the adsorbed water [33,34]. The characteristic bands at 1200–1650 cm⁻¹ correspond to the stretching and rotation vibration of C-N and C=N in heterocycles [35]. The sharp peaks at 808 cm⁻¹ are usually treated as the breathing modes of triazine units (C₆N₇, the building blocks of the g-C₃N₄ structure) [36–38]. Notably, though the peak location and shape are similar, the intensity varies, indicating their different local structures. Specifically, the intensity of the bands at 1200–1650 cm⁻¹ ascribed to aromatic heterocyclic rings obviously weakens on V-pg-C₃N₄ in comparison with that of V-g-C₃N₄ while the intensity of the bands at 3156 cm⁻¹ is almost identical. These results indicate that the addition of HCl in the preparation would cleave some heterocycles in g-C₃N₄. According to the literature [21,39], such cleavage usually promotes the formation of defects sites and terminal N species (e.g., C-NHₓ). Considering the similar bulk structures of V-g-C₃N₄ and V-pg-C₃N₄, the cleavage of heterocycles likely occurred only on the catalyst surface.

To further reveal the influence of protonation on the surface structure of V-pg-C₃N₄, we performed N1s and V2p X-ray photoelectron spectroscopy (XPS) analysis for V-g-C₃N₄ and V-pg-C₃N₄-0.46. As shown in Figure 2a, the high-resolution spectra of N1s can be
deconvoluted into three peaks. The major peak with a binding energy of 398.4 eV is ascribed to triazine nitrogen (C-N=C, Na in Figure 2b) [40]. The second peak at 399.3 eV corresponds to sp\(^3\)-hybridized three-coordinate N species (N-(C)\(_3\) and C-N(-C)-H, Nb in Figure 2b) [41,42], and the peak with the highest binding energy can be assigned to sp\(^3\)-hybridized surface amino groups (e.g., -NH\(_2\) and -NH\(^+\), Nc in Figure 2b) at the edge of g-C\(_3\)N\(_4\) sheets [21,43]. Interestingly, the relative intensities of these peaks are different for V-pg-C\(_3\)N\(_4\)-0.46 and V-g-C\(_3\)N\(_4\), suggesting the different composition of N species. Specifically, the percentage of Na decreases from 0.72 on V-g-C\(_3\)N\(_4\) to 0.59 on V-pg-C\(_3\)N\(_4\)-0.46. This result is consistent with the reduced FT-IR band intensity at 1200–1650 cm\(^{-1}\), suggesting the presence of HCl in the preparation process indeed changes the surface heterocycle structure of C\(_3\)N\(_4\). The percentage of Nb increases from 16% for V-g-C\(_3\)N\(_4\) to 26% for V-pg-C\(_3\)N\(_4\)-0.46 while the percentage of Nc increases from 12% for V-g-C\(_3\)N\(_4\) to 14% for V-pg-C\(_3\)N\(_4\)-0.46, suggesting the cleaved heterocycles were converted into groups with sp\(^3\)-hybridized N species. The changed surface structure of g-C\(_3\)N\(_4\) support eventually alters the surface state of supported vanadia. As shown in Figure 2c, the V\(_2p_{3/2}\) spectra can be deconvoluted into two peaks at 515.3 and 517.1 eV, which are characteristic of V\(^4+\) and V\(^5+\) species, respectively [19]. Notably, the molar ratio of V\(^4+\)/V\(^5+\) changes from 0.31/0.69 for V-g-C\(_3\)N\(_4\) to 0.21/0.79 for V-pg-C\(_3\)N\(_4\)-0.46. This is likely due to the stronger interaction between vanadia and protonated g-C\(_3\)N\(_4\) support in V-pg-C\(_3\)N\(_4\)-0.46 [22]. Specifically, the abundant Nb and Nc species in V-pg-C\(_3\)N\(_4\)-0.46 provide more anchoring sites for vanadia species, which improve the dispersion of vanadia and promote the electron transfer between vanadia and the g-C\(_3\)N\(_4\) support.

**Figure 2.** XPS analysis of V-g-C\(_3\)N\(_4\) and V-pg-C\(_3\)N\(_4\)-0.46 samples. (a) N1s; (b) a possible structure of g-C\(_3\)N\(_4\) reproduced with permission from [21]. Copyright 2018, Elsevier; (c) V2p; (d) the percentage of (Nb + Nc) as a function of X in V-pg-C\(_3\)N\(_4\)-X. 
To quantify the influence of HCl addition on the surface structure of V-pg-C₃N₄-X (X corresponds to mol HCl/mol N), we further investigated the XPS spectra for other V-pg-C₃N₄-X catalysts and plotted the percentage of (N⁺ + N₆) as a function of X. As shown in Figure 2d, the percentage of (N⁺ + N₆) exhibits a volcano plot versus X. Specifically, (N⁺ + N₆)/N increases from 28% for V-g-C₃N₄ (X = 0) and 36% for V-pg-C₃N₄-0.09 (X = 0.09) to 41% for V-pg-C₃N₄-0.46 (X = 0.46), and then decreases to 31% for V-pg-C₃N₄-0.93 (X = 0.93). The maximum (N⁺ + N₆)/N is achieved at X = 0.46, suggesting a proper amount of HCl addition is critical to the surface structure. When X is lower than 0.46, the amount of HCl is too small to change the bulk structure of g-C₃N₄ (Figure 1a). The increase in X would promote the hydrolysis of the aromatic CN heterocycles on the surface of g-C₃N₄ and therefore lead to increased (N⁺ + N₆)/N, but when X is larger than 0.46, the excessive HCl not only hydrolyzes the aromatic CN heterocycles but also promotes the exfoliation of bulk g-C₃N₄. The further increase in X would expose more N₆ on the surface and therefore decrease (N⁺ + N₆)/N. As previously reported in the literature [3,44], the amino groups on the surface can react with VO(acac)₂ to immobilize vanadia species. It is therefore expected that higher vanadia dispersion would be achieved by V-pg-C₃N₄ with larger (N⁺ + N₆)/N. To confirm this hypothesis, we calculated the surface V/N molar ratio. Interestingly, it first increases from to 0.8% for V-pg-C₃N₄-0.05 to 2.1% for V-pg-C₃N₄-0.46 and then decreases to 1.2% for V-pg-C₃N₄-0.92. The similar trend of (N⁺ + N₆)/N and V/N molar ratio confirms that high surface amino groups are beneficial for vanadia dispersion.

2.2. Microstructures of V-g-C₃N₄ and V-pg-C₃N₄

The different surface chemical states are associated with the different microstructures of V-g-C₃N₄ and V-pg-C₃N₄-0.46 (Figure 3). As shown in Figure 3a and 3b, V-pg-C₃N₄-0.46 presents a thin lamellar and platelet-like structure, which is similar to that of g-C₃N₄. Elemental mapping of V-pg-C₃N₄ shows a homogeneous distribution of C, N, and V (Figure 3e). No obvious aggregation of vanadia on the surface of g-C₃N₄ was observed, confirming the high dispersion of vanadia species over the support. In stark contrast, the transmission electron microscope (TEM) and scanning electron microscope (SEM) images of V-g-C₃N₄ exhibit two distinct characters (Figure 3c and 3d). The thin lamellar and platelet-like structures are characteristic of g-C₃N₄ while the nanorods are vanadia. Elemental mapping of V-g-C₃N₄ (Figure 3f) shows an inhomogeneous distribution of C, N, and V elements, which further confirms the phase separation observed by TEM and SEM. The distinct microstructures between V-g-C₃N₄ and V-pg-C₃N₄-0.46 likely originate from the different surface structure and interfacial interaction. According to our previous publications, strong interfacial interaction benefits the high dispersion of precursors on the support surface, eventually leading to the high dispersion of supported nanomaterials. For example, strong electronic interaction between Bi⁵⁺ and ZnO (or TiO₂) [45]. During the following transformation of Bi⁵⁺ into BiO⁺ or Bi₂O₃, the highly dispersed Bi⁵⁺ favors bounded nucleation and growth, which eventually lead to the high dispersion of BiO⁺ or Bi₂O₃ on the supports [46,47]. For g-C₃N₄, the interaction between amino groups and vanadium species is significantly higher than that between triazine nitrogen and vanadium species [4]. When HCl is added to the preparation of V-pg-C₃N₄-0.46, the surface of g-C₃N₄ is protonated and can provide more amino groups to anchor vanadium species. The bounded vanadium precursors in situ convert into vanadia and therefore achieve high dispersion on the surface of protonated g-C₃N₄. In the absence of HCl, the surface amino groups are limited and the interaction between g-C₃N₄ and vanadium species is too weak to drive the high dispersion of vanadium precursors. The free nucleation and growth of vanadium species eventually produce vanadia nanorods that are separated from the g-C₃N₄ support. It is important to highlight that in traditional synthetic methods, the high dispersion of vanadia in V-g-C₃N₄ was usually achieved by increasing the surface area of g-C₃N₄ (e.g., exfoliation or mesopores) [19,21]. In this study, however, the high dispersion of vanadia in V-pg-C₃N₄ was achieved without changing the bulk structure of g-C₃N₄. The similar bulk structure, surface area but distinct vanadia
dispersion between V-g-C_3N_4 and V-g-C_3N_4 suggest the decisive factor for high vanadia dispersion is the surface structure of g-C_3N_4 rather than the surface area.

![Figure 3. TEM (a) and SEM (b) images of V-pg-C_3N_4-0.46; TEM (c) and SEM (d) images of V-g-C_3N_4. Elemental mapping of V-pg-C_3N_4-0.46 (e) and (f) V-g-C_3N_4.](image)

2.3. Catalytic Performance of V-pg-C_3N_4

The catalytic performance of the catalysts was tested in direct hydroxylation of benzene to phenol using H_2O_2 as the oxidant. According to the literature, H_2O_2 was relatively stable in weak acidity conditions [48]. To this end, a mixture of acetonitrile and acetic acid was used as a solvent. Control experiment suggests that both g-C_3N_4 and protonated g-C_3N_4 display no activity in the absence of vanadia species, which is associated with its poor activity in H_2O_2 activation [4]. Interestingly, once vanadia was supported, V-g-C_3N_4 exhibited considerable conversion of benzene, suggesting vanadia species can activate H_2O_2 to hydroxylate benzene. Before evaluating the catalytic performances of different vanadia catalysts, we first optimized the reaction conditions. The optimal reaction temperature is 333 K as it achieves high phenol yield and avoids the volatilization of benzene (boiling point of 353 K). Figure 4a plots benzene conversion and phenol selectivity as a function of reaction time over V-pg-C_3N_4-0.46. The selectivity of phenol is always higher than 95%, which is similar to that for other reported C_3N_4-based catalysts (Table 1). According to the literature [4], the high selectivity of phenol is closely related to the unique structure of C_3N_4. Xu et al. [19] carried out benzene temperature-programmed desorption experiments over g-C_3N_4, V_2O_5, and V/g-C_3N_4 and found that benzene preferred to adsorb on g-C_3N_4 instead of vanadia. Notably, g-C_3N_4 features aromatic s-triazine rings and π electrons, which facilitate a strong planar adsorption of benzene on the surface of g-C_3N_4. However, once the adsorbed benzene is hydroxylated to phenol by H_2O_2, the aromatic ring alters the symmetry of the molecular orbital [17]. The resulting non-planer adsorption of phenol is much weaker than the planer adsorption of benzene. As a result, phenol tends to desorb from g-C_3N_4. The conversion of benzene rapidly increases from 25% to 62% along with the reaction time extension from 1 h to 5 h. Further increasing the reaction to 8 h, the conversion slightly increases to ~70%, likely due to the runout of H_2O_2. To this end, the products of 5-h reaction were used to evaluate the catalytic performance of different catalysts.
Figure 4. (a) Catalytic activity as a function of reaction time over V-pg-C$_3$N$_4$-0.46; (b) Catalytic activity (5 h) as a function of the HCl amount used in the preparation of V-pg-C$_3$N$_4$-X. Reaction conditions: benzene (1.0 mL, 11.3 mmol), hydrogen peroxide (30 wt%, 3.0 mL, 29.6 mmol), acetonitrile (4.8 mL), acetic acid (1.2 mL), catalyst (0.06 g, 0.022 mmol V), T = 333 K. (c) Benzene conversion as a function of (N$_b$ + N$_c$)/N over V-pg-C$_3$N$_4$-X. (d) A possible reaction mechanism for the direct hydroxylation of benzene to phenol over V-pg-C$_3$N$_4$ catalysts.

Figure 4b plots the catalytic performance of V-pg-C$_3$N$_4$-X as a function of X, i.e., the amount of HCl (mol HCl/mol N) used in the preparation of V-pg-C$_3$N$_4$-X. When X = 0, it is also called V-g-C$_3$N$_4$. Interestingly, all V-pg-C$_3$N$_4$ catalysts exhibit higher benzene conversion than V-g-C$_3$N$_4$, suggesting that the addition of HCl in the preparation benefits the catalytic performance. In particular, the benzene conversion over V-pg-C$_3$N$_4$-0.46 is 62%, which is significantly higher than that of V-g-C$_3$N$_4$ (42%). Considering that these two catalysts have similar XRD patterns, surface area, and vanadia loading amount, the mass transfer performances should be the same. Their different catalytic performances most likely originate from their distinct surface structures, especially their different amino contents and vanadia dispersion which influence the activation of H$_2$O$_2$. Second, the catalytic performance of V-pg-C$_3$N$_4$-X exhibits a volcano plot versus X, suggesting the amount of HCl added in the preparation is critical. Interestingly, the plot follows the same trend as that of the volcano plot of (N$_b$ + N$_c$)/N versus X. Specifically, when X is lower than 0.46, (N$_b$ + N$_c$)/N and benzene conversion increase along with the increase in X, but when X exceeds 0.46, they decrease. A maximum of 62% benzene conversion with 60.1% phenol yield is achieved at 333 K over V-pg-C$_3$N$_4$-0.46, a catalyst with the highest (N$_b$ + N$_c$)/N. The mass specific activity of V-pg-C$_3$N$_4$-0.46 is as high as 2.11 g g$^{-1}$ h$^{-1}$, which exceeds most reported results (Table 1). Moreover, when we plot benzene conversion as a function of the percentage of (N$_b$ + N$_c$), a quasi-linear relationship is obtained (Figure 4c). These results are consistent with the hypothesis that high vanadia dispersion enabled by abundant surface amino groups benefits the hydroxylation of benzene to phenol over V-pg-C$_3$N$_4$. 


2.4. Reaction Mechanism of Benzene Hydroxylation over V-pg-C₃N₄

According to the literature [18,19,49], the hydroxylation of benzene to phenol over V-pg-C₃N₄ follows a synergistic mechanism (Figure 4d). Specifically, benzene is adsorbed and activated on the g-C₃N₄ support while H₂O₂ is involved in the V⁴⁺/V⁵⁺ redox cycle. Considering that phenol is produced by the reaction between activated benzene and V⁵⁺–O–O•, the overall reaction rate of benzene hydroxylation depends on both activation reactions. In general, due to the abundant tri-s-triazine moieties and the facile electron transfer from C₃N₄ to benzene, the adsorption and activation of benzene over g-C₃N₄ can easily occur. In contrast, the oxidation of V⁴⁺ into V⁵⁺–O–O• by H₂O₂ may be limited by the number of active vanadia sites. In this study, the surface structure (amino groups and vanadia dispersion) of V-pg-C₃N₄ was regulated without changing the bulk structures, providing an ideal model to investigate the influence of surface structure on the catalytic performance of benzene hydroxylation. According to the above discussion, the addition of HCl in the preparation of V-pg-C₃N₄-X leads to the protonation of g-C₃N₄. The resultant increase in surface amino groups provides more anchoring sites for vanadia species and therefore achieves higher vanadia dispersion. Considering that V-pg-C₃N₄-0.46 has a similar surface area and vanadia loading amount as V-g-C₃N₄, the higher vanadia dispersion means it has more active vanadia sites for H₂O₂ activation, which therefore leads to superior catalytic performance in benzene hydroxylation to phenol.

3. Materials and Methods

3.1. Preparation of g-C₃N₄

g-C₃N₄ was synthesized by the direct pyrolysis of melamine. Briefly, 5.0 g of melamine was placed in a crucible with a cover and then heated at 550 °C for 2 h with a ramping rate of 5 °C min⁻¹.

3.2. Preparation of V-pg-C₃N₄

Typically, 0.3 g of as-synthesized g-C₃N₄ was dispersed into 10 mL of water containing 0.032 g of vanadyl acetylacetonate. After vigorous stirring for 20 min, a certain amount of HCl (ca. 37 wt%) was added to the above mixture dropwise. The mixture was stirred at room temperature for 2 h and subsequently heated at ~80 °C until the solvent was totally evaporated. The obtained product was calcined in the crucible with a cover at 300 °C for 2 h with a ramping rate of 2 °C min⁻¹. The obtained sample was labeled as V-pg-C₃N₄-X, where X (X = 0.05, 0.09, 0.28, 0.46, 0.70, and 0.93) is the molar ratio between HCl and N atom in g-C₃N₄ (mol HCl/mol N). V-g-C₃N₄ was synthesized in the same way as V-pg-C₃N₄-X except that no HCl was added. Inductively coupled plasma mass spectrometry analysis confirmed that the mass loading of V was around 1.5 wt.%.

3.3. Characterizations

Scanning electron microscopy (SEM) images and elemental mapping were obtained using a Hitachi S4800 SEM microscopy equipped with an energy dispersive X-ray spectroscopy (EDS). Transmission electron microscopy investigations were performed on a HT7700 electron microscope. X-ray diffraction patterns were collected using a Rigaku Ultimate IV diffractometer (Cu Kα radiation, 40 kV and 30 mA). Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Nicolet 380 spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Scientific ESCALAB Mark II spectrometer.

3.4. Catalytic Performance Evaluation

The direct hydroxylation of benzene to phenol was performed in a three-neck round-bottom flask equipped with a reflux condenser. Typically, 1 mL of benzene, 4.8 mL of acetonitrile, 1.2 mL of 80 wt.% acetic acid, and 60 mg of catalyst were added to a 25 mL three-necked flask. The solution was stirred at 60 °C for 20 min to ensure adsorption equilibrium of benzene on the catalyst. Then, 3 mL of aqueous H₂O₂ solution (30 wt.%,
29.5 mmol) was dropwise added into the reactor within 2 min under vigorous stirring. The reaction was conducted at 60 °C for 1–8 h. After the reaction, the mixture was separated and the liquid products were analyzed by Shimadzu LC-20AD HPLC with an Ultimate XB-C18 column.

Conversion of benzene (Conv.) and selectivity to phenol (Sel.) were calculated as follows:

\[
\text{Conv.} = \frac{n_{\text{phenol}} + n_{\text{BQ}} + n_{\text{HQ}} + n_{\text{CA}}}{n_{\text{benzene}} + n_{\text{phenol}} + n_{\text{BQ}} + n_{\text{HQ}} + n_{\text{CA}}} \times 100\%
\]

\[
\text{Sel.} = \frac{n_{\text{phenol}}}{n_{\text{phenol}} + n_{\text{BQ}} + n_{\text{HQ}} + n_{\text{CA}}} \times 100\%
\]

where \(n_{\text{benzene}}, n_{\text{phenol}}, n_{\text{BQ}}, n_{\text{HQ}}, n_{\text{CA}}\) are the molar amount (mol) of benzene, phenol, benzoquinone (BQ), hydroquinone (HQ), and catechol (CA).

The mass specific activity for each catalyst was calculated as follows:

\[
\text{Specific activity} \left(g\ h^{-1}g_{\text{cat}}^{-1}\right) = \frac{n_{\text{phenol}} \times M_{\text{phenol}}}{W_{\text{cat}} \times t}
\]

where \(M_{\text{phenol}}, W_{\text{cat}}, t\) represent the formula weight (g mol\(^{-1}\)) of phenol, the mass of overall catalyst (g), and the reaction time (h), respectively.

4. Conclusions

We developed a one-pot synthesis of V-pg-C\(_3\)N\(_4\) which protonates g-C\(_3\)N\(_4\) and loads vanadia simultaneously. Characterizations suggest that the protonation of g-C\(_3\)N\(_4\) in diluted HCl solution facilitates the generation of amino groups (NH/NH\(_2\)) on the surface without changing its bulk structure. The generated amino groups serve as anchoring sites to stabilize the highly dispersed vanadia species, which efficiently activate H\(_2\)O\(_2\) into radical-containing V\(^{5+}\) species to react with the adjacent benzene activated over g-C\(_3\)N\(_4\). Interestingly, the percentage of surface amino groups and the vanadia dispersion can be easily regulated by the amount of HCl added in the preparation. The optimal catalyst, V-pg-C\(_3\)N\(_4\)-0.46, achieves 60% benzene conversion and 99.7% phenol selectivity at 60 °C with H\(_2\)O\(_2\) as the oxidant. The mass-specific activity of V-pg-C\(_3\)N\(_4\)-0.46 is as high as 2.11 g g\(_{\text{cat}}\)\(^{-1}\) h\(^{-1}\), which exceeds most reported results.

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**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

**Conflicts of Interest:** The authors declare no conflict of interest.

**Sample Availability:** Samples of the compounds V-g-C\(_3\)N\(_4\) and V-pg-C\(_3\)N\(_4\) are available from the authors.

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