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Article

Facile synthesis of Fe-containing graphitic carbon nitride materials and their catalytic application in direct hydroxylation of benzene to phenol

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ABSTRACT

Fe-containing graphitic carbon nitride (Fe-g-C₃N₄) materials were synthesized via one-step pyrolysis of FeCl₃ and dicyandiamide. The physicochemical properties of the synthesized Fe-g-C₃N₄ samples were characterized by N₂ adsorption-desorption, X-ray diffraction, thermal gravimetric, Fourier transform infrared, UV-vis diffuse reflectance, X-ray photoelectron spectroscopy, and transmission electron microscopy. The Fe cations were anchored by nitrogen-rich g-C₃N₄, whereas the graphitic structures of g-C₃N₄ were retained after the introduction of Fe. As heterogeneous catalysts, Fe-g-C₃N₄ exhibited good catalytic activity in the direct hydroxylation of benzene to phenol with H₂O₂, affording a maximum yield of phenol of up to 17.5%. Compared with other Fe- and V-containing g-C₃N₄ materials, Fe-g-C₃N₄ features a more convenient preparation procedure and higher catalytic productivity of phenol.

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1. Introduction

As an important commodity chemical, phenol is extensively used for the manufacture of phenol resins, caprolactam, adipic acid, dyestuffs, pesticides [1,2], etc. The three-step cumene process is the main approach for the synthesis of phenol and contributes with more than 90% of the global output of phenol. However, the conventional industrial synthetic route suffers from several drawbacks including high-energy consumption, low one-pass yield of phenol (~5%, based on the initial benzene quantity), and dependence on the market of acetone [3–5]. In the past decade, several new synthetic strategies have

been proposed for the production of phenol. Among them, the direct hydroxylation of benzene, featuring an environmentally benign procedure, has been commonly proposed as the catalytic process with the most potential for the manufacture of phenol [3,6].

A series of oxidant agents including air, oxygen, N₂O, and H₂O₂ have been employed for the direct hydroxylation of benzene [7,8]. Although either air or oxygen is very cheap and widely available, the catalytic activity in such a process is very low and far from industrial implementation [9]. Furthermore, the main restriction for the industrial implementation of N₂O is its complicated operational technology [3]. In contrast, the use

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of H₂O₂ as an oxidant for the transformation from benzene to phenol demands milder reaction conditions together with a simpler process than its counterparts. Simultaneously, water is, ideally, the sole co-product [10]. Therefore, the direct hydroxylation of benzene under H₂O₂ has received tremendous attention in the field of phenol synthesis. Nevertheless, phenol can be over-oxidized to produce hydroquinone and benzoquinone. In this sense, it is still a hot topic to develop a robust catalyst that can provide excellent activity along with high selectivity to the target molecule.

A variety of heterogeneous catalysts, including titanium silicalite sieves (TS-1) [11,12], heteropolyacids (HPAs) [2,5,6], metal oxides supported on mesoporous materials [1,2,13], and transition metals incorporated into molecular sieves [7], have been extensively employed for the direct hydroxylation of benzene. In the past decade, graphitic carbon nitride (g-C₃N₄) has attracted tremendous attention as a new type of catalyst in both thermal catalysis [14,15] and photocatalysis [16,17]. In particular, because of its unique capacity to activate the benzene molecule, g-C₃N₄ (especially mesoporous g-C₃N₄) has demonstrated potential catalysis in several benzene-involved reactions, including alkylation [18], acylation [19,20], and oxidation of benzene [21–23]. Recently, our group has synthesized mesoporous g-C₃N₄ materials, which were then loaded with vanadyl(IV) acetylacetonate [VO(acac)₂] [24] and vanadia [8]. The results showed that such g-C₃N₄-based composites were able to promote the direct hydroxylation of benzene under H₂O₂, with a maximum yield of phenol of about 18%.

Although mesoporous g-C₃N₄ catalysts possessed high surface areas and exhibited promising catalysis in benzene-activating reactions, all the reported mesoporous g-C₃N₄ supports have been prepared by a nanocasting method, with silica materials as hard templates [19,25,26]. This preparation demanded a silica-etching procedure with a volatile and toxic HF or NH₄HF₂ solution, which was time-consuming and not environmentally friendly [15,27,28]. To circumvent these issues we, very recently, developed vanadia catalysts supported on exfoliated g-C₃N₄ nanosheets, which were more conveniently synthesized than mesoporous g-C₃N₄ [29]. However, the final catalytic activity of such catalysts in the hydroxylation of benzene is still not satisfactory. On the other hand, the transition metal halides represented by FeCl₃, are the typical Lewis acids which are extensively used in benzene-activating reactions [30,31]. In this work, a facile and rapid method to prepare Fe-containing g-C₃N₄ materials was developed via one-step pyrolysis of FeCl₃ and dicyandiamide. As heterogeneous catalysts, the Fe-g-C₃N₄ materials catalyzed the direct hydroxylation of benzene under H₂O₂ with good catalytic activities, affording a maximum yield of phenol of as much as 17.5% at a reaction time of 2 h.

2. Experimental

2.1. Catalyst preparation

FeCl₃ (0.15 g) and dicyandiamide (DCDA, 4.00 g) were added into 100 mL of ethanol, and then refluxed at 80 °C for 3 h.

The solution was dried at 60 °C until removal of ethanol and formation of a dark yellow solid. After being ground, the yellow powder was calcined under N₂ atmosphere at 550 °C for 4 h, and the resultant solid was designated as *m*Fe/g-C₃N₄ catalyst, where *m* indicated the weight percentage of Fe of g-C₃N₄.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were collected on a D8 Advance (Bruker) X-ray diffractometer equipped with a graphite monochromator (40 kV, 40 mA) using Ni-filtered Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$).

Nitrogen adsorption and desorption measurements were carried out at –196 °C using an ASAP 2020 (Micromeritics) porosimeter. Before the measurement, the samples were degassed ($1.33 \times 10^{-2} \text{ Pa}$) at 150 °C for 4 h. The specific surface areas were calculated using the Brunauer–Emmet–Teller (BET) method, and the pore size distributions were determined by the Barret–Joyner–Halenda (BJH) model, from the desorption branches.

Fourier transform infrared (FT-IR) spectra in transmission mode were analyzed on a Tensor 27 (Bruker) spectrometer with the aid of KBr pellets. Each spectrum was measured with a resolution of 4 cm^{–1} and recorded at room temperature.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a PHI 5000C (Perkin–Elmer) spectrometer recording in the constant energy mode (Mg K α radiation as the excitation source).

UV–vis diffuse reflectance spectra (DRS) were recorded in a UV-3600 (Shimadzu) spectrophotometer. The UV–vis spectra used BaSO₄ as the standard reference.

Thermal gravimetric (TG) tests were performed on a TGA 7 (Perkin–Elmer) thermogravimetric analyzer. The specimens were heated, under a flow of air, from 50 to 800 °C with a ramping rate of 20 °C min^{–1}.

Transmission electron microscopy (TEM) images were obtained on a Tecnai G2 F20 S-TWIN microscope operated at 200 kV. Energy dispersive X-ray spectra (EDS) and elemental mapping were performed on the equipped Oxford X-Max 80T detector.

2.3. Catalytic evaluation

The catalytic reactions were evaluated in a round-bottom flask. Benzene (1 mL, 11.2 mmol) and solvent (5 mL of acetonitrile and 1 mL of acetic acid) were mixed well, followed by the addition of the catalyst. After the temperature of the mixture reached 60 °C, 3 mL of H₂O₂ (a.q., 30 wt%) were continuously fed into the flask through a peristaltic pump (the addition of H₂O₂ lasted for ~30 min). During the reaction, a small amount of reaction mixture (< 0.15 mL) was periodically collected and centrifuged. The liquid phase was analyzed by gas chromatography using an SE-54 capillary column. The conversion (Conv.) of benzene and selectivity (Sel.) for phenol were calculated by means of an area-normalization method, and the detailed calculation equations were as follows:

$$Conv. = \frac{n_{\text{phenol}} + n_{\text{benzoquinone}}}{n_{\text{benzene}} + n_{\text{phenol}} + n_{\text{benzoquinone}}}$$

$$Sel. = \frac{n_{\text{phenol}}}{n_{\text{phenol}} + n_{\text{benzoquinone}}}$$

3. Results and discussion

3.1. Catalyst characterization

The textural properties of the g-C₃N₄ and Fe-g-C₃N₄ materials were initially measured by N₂ adsorption-desorption characterization. The g-C₃N₄ presents a type-IV isothermal curve (Fig. 1), along with a H3 hysteric loop in the range of $p/p_0 = 0.8-0.99$, suggesting that the bare sample contains mesoporous structures. Notwithstanding, the total pore volume as well as the surface area measured from g-C₃N₄ are very low (Table 1). Comparatively, the incorporation of Fe into g-C₃N₄ effectively improves the surface area and total pore volume. In the case of 10.0Fe-g-C₃N₄, the pore volume and surface area are 0.25 cm³ g⁻¹ and 56 m² g⁻¹, respectively. However, with further increases in the amount of Fe, the textural parameters of Fe-g-C₃N₄ decrease.

Fig. 2 presents the XRD profiles of the bulk g-C₃N₄ and Fe-g-C₃N₄ composites. The pure g-C₃N₄ presents a sharp diffraction peak at $2\theta = 27.4^\circ$ ($d = 0.375$ nm). This peak is indexed as (002) planes, i.e. the interplanar stacking structure of graphitic material [19,32]. Furthermore, a small peak with weak intensity is found at $2\theta = 13.2^\circ$ ($d = 0.776$ nm), corresponding to an in-plane structural packing motif (i.e. hole-to-hole array of the nitride pores) [19]. As for the Fe-g-C₃N₄ materials, the intensity of the (002) peaks becomes much weaker, while their (100) peaks seem to disappear. The comparison suggests that after incorporation of Fe, the crystallinity of the graphitic structure of g-C₃N₄ is drastically decreased. Moreover, the position of the (002) diffraction peaks of the Fe-g-C₃N₄ composites moves toward higher values of 2θ (the inset of Fig. 2), indicating that the introduction of Fe probably results in the shrinkage

Table 1

Textural parameters of the g-C₃N₄ and Fe-g-C₃N₄ materials.

Sample	S_{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
g-C ₃ N ₄	10	0.05
2.5Fe-g-C ₃ N ₄	8	0.22
5.0Fe-g-C ₃ N ₄	48	0.17
7.5Fe-g-C ₃ N ₄	49	0.27
10.0Fe-g-C ₃ N ₄	56	0.25
12.5Fe-g-C ₃ N ₄	18	0.22

of the graphitic interlayers of g-C₃N₄.

It is of interest to mention that we previously reported the fabrication of MgO/g-C₃N₄ materials starting from Mg(NO₃)₂ and DCDA [33]. The synthetic route of these materials was very similar to this work. By contrast, the position of the primary (002) peak obtained in MgO/g-C₃N₄ was much lower than that of the pure g-C₃N₄ sample. We surmise that the difference in terms of the d spacing value of the graphitic interlayers lies in the precursor of the metal salts. In other words, during the pyrolysis of DCDA to g-C₃N₄, Mg(NO₃)₂ also underwent decomposition and released a large amount of gas, leading to the expansion of the graphitic layers. In comparison, in the case of Fe-g-C₃N₄, although the reaction between FeCl₃ and g-C₃N₄ for the formation of g-C₃N₄ would also generate gas (such as HCl), the shrinkage and/or collapse of the graphitic layers of g-C₃N₄ may occur dominantly, which might be responsible for the abovementioned decrease of crystallinity of g-C₃N₄ after the introduction of Fe.

The morphology of the materials was observed by TEM. The low-resolution images of 7.5Fe-g-C₃N₄ (Fig. 3(A) and (C)) reveal apparent worm-like structures. From these two TEM images, the mean size of most of such pores is much larger than 50 nm. The high-resolution image (Fig. 3(B)) displays thin-layer morphology; however, no obvious particles have been detected in the images. Moreover, the EDS mapping images of 7.5Fe-g-C₃N₄ verify that the carbon, nitrogen, and iron elements are well dispersed on the material. In contrast, the oxygen element shows irregular distribution on the surface of

Fig. 1. N₂ adsorption-desorption isotherms of the g-C₃N₄ and Fe-g-C₃N₄ materials.

Fig. 2. XRD patterns of the g-C₃N₄ and Fe-g-C₃N₄ materials.

Fig. 3. TEM images (A–C) of 7.5Fe-g-C₃N₄ and the corresponding EDS mapping images of the carbon (D), nitrogen (E), and iron (F) elements.

7.5Fe-g-C₃N₄ (Fig. S1), excluding the formation of iron oxide on the Fe-g-C₃N₄ materials.

The TG curves of various materials are illustrated in Fig. S2. The pure g-C₃N₄ shows good thermal stability below 500 °C while undergoing significant weight loss in the range of 550–750 °C, due to its decomposition. The introduction of Fe into g-C₃N₄ obviously undermines the thermal stability, making the decomposition temperature much lower. According to the values of the residual weight obtained at 750 °C (the final solid is Fe₂O₃), the loading amount of Fe in the various Fe-g-C₃N₄ samples can be estimated. As listed in Table S1, the content of acquired-Fe in 7.5Fe-g-C₃N₄ is ~1.0 mmol g_{catal}^{−1}, and the contents of Fe for the other materials correlate well with their

nominal loading amounts.

The chemical functionalities of the materials were analyzed by FT-IR. All the spectra exhibit three major band zones (Fig. 4). The broad bands centered at ~3165 cm^{−1} are attributed to the uncondensed amino functionalities (−NH₂ and −NH−) at the edges of the graphitic layers of g-C₃N₄ [34] and to the O–H derived from the absorbed surface water. The multiple bands appearing from 1600 to 1200 cm^{−1} correspond to the stretching modes of the nitrogen heterocycles (i.e. triazine or tri-s-triazine) [32], while the high-intensity sharp peaks located at 804 cm^{−1} are assigned to the breathing mode of triazine-based sheets of g-C₃N₄. Compared with the spectrum of g-C₃N₄, in the case of Fe-g-C₃N₄ the intensity of the peaks associated with the CN heterocycles clearly decreases with the increment of Fe content. This phenomenon signifies that the tectonic units of tri-s-triazine of g-C₃N₄ were damaged, possibly due to the interaction between iron and the N species of g-C₃N₄ [35]. Furthermore, a distinct peak emerges at 2164 cm^{−1} for each Fe-g-C₃N₄, which, however, cannot be observed in the FT-IR spectrum of g-C₃N₄. These unique transmission signals have also been found in the spectra of Fe- and Zn-doped g-C₃N₄ materials previously reported by other groups [36,37], and were indexed as C≡N bonds converted from *sp*²-hybridized C–N bonds, thus further verifying the steady interaction between Fe and g-C₃N₄, in the Fe-g-C₃N₄ materials.

Fig. 4. FT-IR spectra of the g-C₃N₄ (a), 2.5Fe-g-C₃N₄ (b), 5.0Fe-g-C₃N₄ (c), 7.5Fe-g-C₃N₄ (d), and 10.0Fe-g-C₃N₄ (e) materials.

The XPS technique was further employed to probe the chemical bonding states on the surface of the materials, and the survey spectra are presented in Fig. S3. The spectrum of g-C₃N₄ shows the signals of carbon and nitrogen, along with a minor peak assigned to the oxygen element (coming from the adsorbed water molecules). The molar ratio of C/N is ~0.71, with higher nitrogen content than the theoretical value of the ideal

Fig. 5. Fe 2p XPS spectra of the FeCl₃ (a), 2.5Fe-g-C₃N₄ (b), and 7.5Fe-g-C₃N₄ (c) materials.

g-C₃N₄ (0.75). This difference is due to the existence of uncondensed terminal amino groups of g-C₃N₄ [33,38], which are also revealed in the above FT-IR spectra. Besides those of the carbon, nitrogen, and oxygen elements, two peaks appear at ~712 and 201 eV in the spectrum of each Fe-g-C₃N₄ sample, which are indicative of Fe 2p and Cl 2p, respectively. Furthermore, the peak intensity of oxygen shows remarkable enhancement with the increment of Fe in the g-C₃N₄ sample. This behavior should be attributed to the partial hydrolysis of FeCl₃ on the surface of g-C₃N₄, which is also observed in the spectrum of the pure FeCl₃ compound.

The fine XPS spectra of Fe 2p for the Fe-g-C₃N₄ materials, as well as for FeCl₃, are given in Fig. 5. The spectrum of FeCl₃ exhibits two binding peaks centered at 725.1 and 712.0 eV, ascribed to the signals of the 2p_{1/2} and 2p_{3/2} orbits, respectively. By comparison, the peaks acquired in the Fe-g-C₃N₄ samples shift to lower binding energies. Interestingly, the average peak position (711.4 eV) of the 2p_{3/2} orbit of Fe-g-C₃N₄ resembles the value reported for Fe(III) porphyrin. In that compound, the Fe center is coordinated by N₄-tetradentate ligands and a chlo-

ride anion [39]. As proposed by Wang et al. [40], g-C₃N₄ built up by tri-s-triazine rings as tectonic units contains abundant “nitrogen pots” (also called “nitrogen holes”), very similarly to other nitrogen-enriched π -conjugated macrocyclic compounds, such as porphyrin and phthalocyanine. Accordingly, the g-C₃N₄ material possessing this similar nitrogen pots has an innate ability to coordinate or anchor transition-metal species (e.g. Fe and Zn). Therefore, it is reasonable to surmise that there is a potential interaction between Fe and the nitrogen species of g-C₃N₄ [23,40]. More specifically, the Fe cations are anchored by nitrogen-rich g-C₃N₄ through Fe–N bonds. However, given the Cl signals revealed in Fig. S3, a certain amount of Fe species ought to exist as FeCl₃.

In order to further analyze the chemical bonding information of the g-C₃N₄ and Fe-g-C₃N₄ materials, deconvolution of the N 1s signals of the g-C₃N₄, 2.5Fe-g-C₃N₄, and 7.5Fe-g-C₃N₄ samples was performed (Fig. 6). Each spectrum could be separated into three independent peaks, i.e. three types of N atoms. The dominance of the N 1s spectrum with the lowest binding energy (398.8 $\pm$ 0.2 eV) is indexed as the sp²-hybridized nitrogen (N_a), existing as C–N=C groups in the tri-s-triazine rings. The peak located at 399.8 $\pm$ 0.2 eV is associated with the sp²-hybridized nitrogen atoms (N_b, C–NH–C and C–N(C)–C) which bridge two or three tri-s-triazine units. The peak with the highest binding energy (401.2 $\pm$ 0.2 eV) corresponds to the uncondensed terminal amino groups (N_c, –NH₂ and –NH–) which have been revealed in the above FT-IR spectra (Fig. 4). The detailed molar distributions of the various nitrogen species for the three samples are summarized in Table S2. The percentages of N_a and N_b atoms of g-C₃N₄ are 69.0% and 22.5%, respectively. The incorporation of FeCl₃ leads to the variation of the distribution of nitrogen species. That is, the percentages of the N_a species decrease while those of the N_b species increase drastically from the g-C₃N₄ to the Fe-g-C₃N₄ samples. Such a change has been observed for Zn-doped g-C₃N₄ materials reported by our [28] and other groups [41]. The increase of the bridging nitrogen species is probably originated from the reaction between FeCl₃ and the N_a atoms in the conjugated

Fig. 6. N 1s XPS spectra of the g-C₃N₄ (A), 2.5Fe-g-C₃N₄ (B), and 7.5Fe-g-C₃N₄ (C) materials.

Fig. 7. UV-vis spectra of the $g\text{-C}_3\text{N}_4$, $2.5\text{Fe-g-C}_3\text{N}_4$, $5.0\text{Fe-g-C}_3\text{N}_4$, $7.5\text{Fe-g-C}_3\text{N}_4$, $10.0\text{Fe-g-C}_3\text{N}_4$, and $12.5\text{Fe-g-C}_3\text{N}_4$ samples.

tri-s-triazine rings of $g\text{-C}_3\text{N}_4$. Such a reaction directly results in the partial breakage of the tri-s-triazine motifs (also as observed in the above FT-IR spectra) and the formation of more bridging N_b species. On the other hand, a certain amount of Fe species is included by adjacent nitrogen species.

UV-vis diffuse reflectance spectra of the $g\text{-C}_3\text{N}_4$ and $\text{Fe-g-C}_3\text{N}_4$ specimens are displayed in Fig. 7. The spectrum of the pristine $g\text{-C}_3\text{N}_4$ shows a major optical absorption with a cutting edge at ~ 457 nm, corresponding to a band gap of ~ 2.7 eV. The absorption is derived from the band gap between HOMO and LUMO in the polymeric melon units of $g\text{-C}_3\text{N}_4$ [42]. A remarkable red shift is detected for each $\text{Fe-g-C}_3\text{N}_4$ material. More specifically, with the increment of Fe content, the band gap is moved progressively towards longer wavelengths. The red shift results from the variation of the electronic structure of $g\text{-C}_3\text{N}_4$, arising from the incorporation of Fe into the skeleton of $g\text{-C}_3\text{N}_4$, i.e. $d\text{-}p$ repulsion between Fe $3d$ and N $2p$ orbitals [35]. Indeed, similar results have also been observed in other $g\text{-C}_3\text{N}_4$ materials doped by Fe [35,43], Zn [28,40,44], and other transition metals [23].

Table 2

Catalytic results of the hydroxylation of benzene to phenol under various materials ^a.

Entry	Catalyst	Conv. (%)	Sel. (%)	Catalytic productivity ^c ($\text{g h}^{-1} \text{g}_{\text{cat}}^{-1}$)
1 ^b	—	—	—	—
2	$g\text{-C}_3\text{N}_4$	—	—	—
3	FeCl_3	12.2	>99	1.29
4	$2.5\text{Fe-g-C}_3\text{N}_4$	6.8	>99	0.72
5	$5.0\text{Fe-g-C}_3\text{N}_4$	13.7	>99	1.44
6	$7.5\text{Fe-g-C}_3\text{N}_4$	17.5	>99	1.84
7	$10.0\text{Fe-g-C}_3\text{N}_4$	13.9	>99	1.46
8	$12.5\text{Fe-g-C}_3\text{N}_4$	10.7	>99	1.13

^a Reaction conditions: 11.2 mmol of benzene, 3 mL of aqueous H_2O_2 solution (30 wt%), 1 mL of acetic acid and 5 mL of acetonitrile as solvents, 50 mg of the catalyst, $T = 60^\circ\text{C}$, and $t = 2$ h.

^b Without any catalyst.

^c Determined by the mass of phenol per gram of overall catalyst per hour.

3.2. Catalyst activity

Initially, a blank test of the hydroxylation of benzene without any catalyst was carried out, and no benzene was converted (Table 2). Likewise, in the presence of pure $g\text{-C}_3\text{N}_4$, no phenol or other product has been detected. Using FeCl_3 instead, the benzene conversion is 12.2% and the selectivity to the target phenol is higher than 99%. Obviously, as a Lewis base, FeCl_3 can promote the reaction. Despite its good catalytic activity, FeCl_3 itself is dissolved in the reaction liquid. In a homogeneously catalytic reaction, it is relatively difficult to separate the catalyst from the liquid phase and then recycle it. $\text{Fe-g-C}_3\text{N}_4$ catalysts show apparent catalytic activity in the hydroxylation reactions, and with an increase of the Fe content, the benzene conversion is remarkably improved. Furthermore, no by-product (e.g. benzoquinone) was detected. Among the $\text{Fe-g-C}_3\text{N}_4$ materials, $7.5\text{Fe-g-C}_3\text{N}_4$ demonstrated the highest catalytic activity, affording a maximum yield of phenol in 2 h under 60°C .

Fig. 8 shows the influence of the reaction conditions on the results of the catalytic hydroxylation of benzene. At a low reaction temperature of 50°C (Fig. 8(A)), the benzene conversion obtained at 2 h of reaction time is $\sim 8.5\%$ and the selectivity to phenol is higher than 99%. As the reaction temperature is elevated, the conversion is improved and reaches its maximum at 60°C . However, further raising of temperature would lead to a gradual decline of catalytic activity, which should be due to the rapid decomposition of H_2O_2 at higher reaction temperature. Fig. 8(B) plots the results of the catalytic hydroxylation of benzene during 3 h. It can be found that the conversion increases continuously yet levels off after 2 h. Moreover, the selectivity to phenol collected across the reaction process is above 99%.

In addition to the reaction temperature and time, the dependence of catalytic performance on catalyst amount and content of H_2O_2 was further investigated using $7.5\text{Fe-g-C}_3\text{N}_4$ as a catalyst. As described in Fig. S4, in the presence of only 25 mg of the catalyst, the phenol yield reaches $\sim 11.0\%$. Further increasing the amount of the catalyst could produce much higher

Fig. 8. Influence of temperature (A) and time (B) on the catalytic performance of $7.5\text{Fe-g-C}_3\text{N}_4$. Reaction conditions: benzene 1.0 mL, H_2O_2 3.0 mL, solvent 6.0 mL, catalyst 50 mg, 2 h (A), 60°C (B).

yields of phenol. Whereas, the use of an excessive amount of the catalyst depresses the catalytic productivity. One possible reason for this behavior is the decomposition of H_2O_2 . Similar phenomena have been previously detected in the same reactions catalyzed by vanadium-doped $\text{g-C}_3\text{N}_4$ [4] and polyoxometalate [6] materials. Furthermore, in the catalytic reactions using various amounts of benzene, the highest phenol yield was obtained in the presence of 1.0 mL of benzene (Table S3).

To examine the reproducibility of the $\text{Fe-g-C}_3\text{N}_4$ catalysts, we used $7.5\text{Fe-g-C}_3\text{N}_4$ as a representative catalyst and evaluated its catalytic performance in consecutive runs. After each test, the catalyst was immediately filtrated, washed with ethanol, and used for the subsequent evaluation. As revealed in Fig. 9, during the five consecutive catalytic runs, the phenol yields are $\sim 17\%$, without any significant decline. Like $7.5\text{Fe-g-C}_3\text{N}_4$, the $5.0\text{ Fe-g-C}_3\text{N}_4$ sample also shows stable catalytic activity during its recycling tests (Fig. S5), suggesting that the $\text{Fe-g-C}_3\text{N}_4$ catalysts have good catalytic reproducibility.

As noted above, due to its innate capacity to activate benzene molecules, $\text{g-C}_3\text{N}_4$ and the $\text{g-C}_3\text{N}_4$ -based materials have been recently employed as catalyst supports for many hydroxylation reactions of benzene to phenol. The catalytic performance of $7.5\text{Fe-g-C}_3\text{N}_4$ in this work is compared with those obtained over other V- and Fe-containing $\text{g-C}_3\text{N}_4$ catalysts, which are summarized in Table 3. It is noted that all the entries are collected from papers published in the past five years. Actually, the reaction conditions including temperature, time, and feeding volume of benzene for each entry are very similar with others. In the case of V-containing $\text{g-C}_3\text{N}_4$, the highest specific productivity ($1.57\text{ g h}^{-1}\text{ g}_{\text{cat}}^{-1}$) is offered by $\text{V/mp-C}_3\text{N}_4$ (entry 3); although for this outstanding activity, the catalyst support (as well as that of entry 5) is mesoporous $\text{g-C}_3\text{N}_4$, which was fabricated by a complicated hard-templating method. As for Fe-containing $\text{g-C}_3\text{N}_4$, entry 5 shows the highest yield of phenol (21.6%); however, the reaction proceeded under light-assisted conditions ($\lambda > 420\text{ nm}$). It is of interest to further compare the catalytic results of entries 6 and 7. In fact, both of these catalysts are prepared using FeCl_3 as a precursor of Fe. We surmise that the significant difference in their catalytic activity might be due to the choice of the precursor of $\text{g-C}_3\text{N}_4$. The former uses urea as a starting material for $\text{g-C}_3\text{N}_4$ while the latter is synthesized based on DCDA. Compared with DCDA, the transformation of urea to the final $\text{g-C}_3\text{N}_4$ would release much more gas

Fig. 9. Catalytic performances of $7.5\text{Fe-g-C}_3\text{N}_4$ during four consecutive runs. Reaction conditions: benzene 1.0 mL, H_2O_2 3.0 mL, solvent 6.0 mL, catalyst 50 mg, 2 h, 60°C .

due to the more drastic self-decomposition of urea, resulting in abundant incompletely condensed tri-s-triazine units with a low degree of polymerization [38,47]. Consequently, less Fe species could not be anchored and were further dispersed by $\text{g-C}_3\text{N}_4$, in the case of entry 6. In contrast, $7.5\text{Fe-g-C}_3\text{N}_4$ in this work exhibits superior catalytic productivity of phenol. Additionally, such $\text{Fe-g-C}_3\text{N}_4$ materials could be easily and rapidly prepared.

4. Conclusions

In summary, Fe-containing $\text{g-C}_3\text{N}_4$ materials have been synthesized by a rapid and simple approach. The graphitic structures of $\text{g-C}_3\text{N}_4$ have remained after the introduction of Fe, and the synthesized $\text{Fe-g-C}_3\text{N}_4$ materials possess surface areas of $8\text{--}56\text{ m}^2\text{ g}^{-1}$. The Fe cations are anchored by nitrogen-abundant $\text{g-C}_3\text{N}_4$ via Fe–N bonds, with a minor charge balanced by chloride anions. In the hydroxylation of benzene in the presence of H_2O_2 , $\text{Fe-g-C}_3\text{N}_4$ samples as heterogeneous catalysts, show much higher catalytic activity than the pure $\text{g-C}_3\text{N}_4$. Under optimized reaction conditions, the maximum yield of phenol is up to 17.5% at 60°C . Compared with other Fe- and vanadia-containing $\text{g-C}_3\text{N}_4$ materials, $\text{Fe-g-C}_3\text{N}_4$ features more facile preparation along with higher catalytic productivity of phenol.

Table 3

Comparison of the hydroxylation reactions of benzene catalyzed by various V- and Fe-containing $\text{g-C}_3\text{N}_4$ catalysts.

Entry	Catalyst	Benzene (mL)	H_2O_2 (mL)	Catalyst (mg)	T ($^\circ\text{C}$)	t (h)	Yield (%)	Catalytic productivity ^a ($\text{g h}^{-1}\text{ g}_{\text{cat}}^{-1}$)
1	$\text{V/g-C}_3\text{N}_4$ [45]	1.0	3.5	40	70	4	17.8	1.16
2	$0.4\text{V-g-C}_3\text{N}_4$ [4]	1.0	3.0	60	60	6	17.7	0.52
3	$\text{V/mp-C}_3\text{N}_4$ ^b [46]	1.5	3.0	60	60	3	17.9	1.57
4	$\text{VO-peg-C}_3\text{N}_4$ ^c [29]	1.0	3.0	75	60	4	11.7	0.40
5	$10\text{FeCl}_3/\text{mpg-C}_3\text{N}_4$ ^b [30]	0.4	0.25	25	60	4	21.6	0.91
6	$\text{Fe-g-C}_3\text{N}_4$ [4]	1.0	3.0	48	60	6	2.3	0.08
7	$7.5\text{Fe-g-C}_3\text{N}_4$	1.0	3.0	50	60	2	17.5	1.84

^a Determined according to the mass of obtained phenol per gram of overall catalyst per hour.

^b Supported on mesoporous $\text{g-C}_3\text{N}_4$ materials.

^c Supported on exfoliated $\text{g-C}_3\text{N}_4$ nanosheets.

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Graphical Abstract

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Facile synthesis of Fe-containing graphitic carbon nitride materials and their catalytic application in direct hydroxylation of benzene to phenol

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Fe-containing graphitic carbon nitride materials were synthesized via one-step pyrolysis. Fe species are anchored and well dispersed on the g-C₃N₄ support, which showed superior catalytic activity in the catalytic hydroxylation of benzene to phenol.

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简便方法合成含铁石墨相氮化碳材料及其催化苯直接羟基化制苯酚

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摘要: 苯酚是一种重要的基本有机化工原料. 全球近 90% 的苯酚都是经“三步异丙苯法”工艺合成而得, 但是该工艺存在单程苯酚收率低 (<5%)、酸污染严重等不足. 同时由于联产丙酮, 苯酚的产量也受丙酮市场所制约. 由苯经氧化或羟基化一步法合成苯酚是催化化学领域中一项极具挑战的课题. 由于苯分子较难活化, 而苯酚易于深度氧化, 因此研发和设计具有高活性和高选择性的催化剂是该课题的研究核心.

因具有诸多特殊的理化性质, 石墨相氮化碳 (g-C₃N₄) 作为一种新型碳质材料近年来在光催化、热催化、燃料电池和气体吸附等领域展示出广阔的应用前景. g-C₃N₄ 的类石墨层基本单元为大π共轭的三均三嗪环, 对苯分子具有良好的吸附和活化能力. 目前, g-C₃N₄ (尤其是具有高比表面的介孔材料) 在苯 Friedel-Crafts 烷基化和酰基化反应、苯的 CO₂ 氧化等反应中均显示了良好的催化活性. 尽管如此, 由于缺乏合适的氧化活性中心, 纯的 g-C₃N₄ 对苯直接羟基化几乎无催化活性.

本课题组曾将乙酰丙酮氧钒和氧化钒负载至介孔 g-C₃N₄, 发现该类催化剂在 H₂O₂ 参与的苯直接羟基化反应中, 苯转化率高达 18%, 而苯酚选择性大于 95%. 然而, 此类介孔 g-C₃N₄ 均采用硬模板法合成, 制备周期长且需要 HF 溶液蚀刻氧化硅模板. 另外, 钒基组分在介孔 g-C₃N₄ 表面也存在着部分溶脱现象.

本文以 FeCl₃ 和二氰二胺为前驱体, 通过一步热解法直接合成了含铁的 g-C₃N₄ 材料 (Fe-g-C₃N₄). 采用 N₂ 吸附-脱附、XRD、TG、FT-IR、UV-vis、XPS 光谱和 TEM 对材料的理化性质进行表征. 结果显示, Fe 的原位引入能显著提高 g-C₃N₄ 的比表面积和孔体积, 且使其依然保持石墨相结构. 同时, 富 N 的 g-C₃N₄ 材料能有效地锚定 Fe 离子, 使其均匀地分散在载体表面. 作为多相催化剂, Fe-g-C₃N₄ 在 H₂O₂ 环境下对苯羟基化合成苯酚的反应表现出较高的催化活性. 当反应温度为 60 °C, 其苯酚收率最高可达 17.5%, 且回收使用多次催化剂活性表现稳定. 与之前报道的含铁和负载氧化钒或乙酰丙酮氧钒的 g-C₃N₄ 催化剂材料相比, Fe-g-C₃N₄ 催化剂制备工艺更加简便.

关键词: 苯; 羟基化; 石墨相氮化碳; 苯酚

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