



# Direct catalytic hydroxylation of benzene to phenol catalyzed by vanadia supported on exfoliated graphitic carbon nitride



Jie Xu\*, Ye Chen, Ying Hong, Huan Zheng, Dan Ma, Bing Xue\*, Yong-Xin Li

Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, School of Petrochemical Engineering, Changzhou University, Gehu Road 1, Changzhou, Jiangsu 213164, PR China

## ARTICLE INFO

### Keywords:

Graphitic carbon nitride  
Benzene  
Hydroxylation  
Vanadia

## ABSTRACT

Direct hydroxylation of benzene is a sustainable and promising strategy to synthesize phenol. The key topic for the catalytic process is the development of an efficient heterogeneous catalyst. In this work, graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ) material was exfoliated and protonated, and then utilized as a support to load vanadia by using  $\text{VO}(\text{acac})_2$  as a precursor. The synthesized materials were characterized by several techniques including  $\text{N}_2$  adsorption–desorption, XRD, TG, TEM, SEM, FT-IR, UV–vis, and XPS. The results exhibited that the exfoliation as a simple method could improve the surface area and pore volume of  $g\text{-C}_3\text{N}_4$ , while protonation was able to facilitate to increase the loading amount of vanadia. In hydroxylation of benzene to phenol in the presence of  $\text{H}_2\text{O}_2$ , the vanadia catalysts supported on  $\text{peg-C}_3\text{N}_4$  demonstrated superior catalytic activity to the catalysts supported on the pristine  $g\text{-C}_3\text{N}_4$ . Moreover, the effects of protonation conditions including acid concentration and temperature on the final catalytic activity have also been investigated. Under optimized conditions, a maximum yield of phenol reached 15% at 60 °C.

## 1. Introduction

Phenol is an important commodity chemical in contemporary chemical industry. As a crucial building block, phenol is extensively employed in the manufacture of resins, fibers, medicines, etc [1]. Currently, the prevailing industrial synthesis of phenol is three-step cumene process invented by Hock et al. dating back to 1940s [2,3], which contributes to more than 90% of worldwide phenol production [1,3]. Unfortunately, the classical synthetic approach suffers from several disadvantages including severe pollution of acid catalysts, low one-pass yield (~5%) of phenol [1], and concomitant dependence on the by-product of acetone [4]. To circumvent these issues, numerous synthetic techniques have been proposed but to date, the direct catalytic hydroxylation of benzene has been commonly regarded as a promising and sustainable strategy for the green synthesis of phenol [5,6].

Oxygen ( $\text{O}_2$ ), nitrous oxide ( $\text{N}_2\text{O}$ ) and  $\text{H}_2\text{O}_2$  are three typical oxidants applied for the transformation of benzene to phenol [7].  $\text{O}_2$  is cheap and widely available; however it demands high reaction temperature, which may induce deep oxidation of benzene. In the case of  $\text{N}_2\text{O}$ , despite its high selectivity to phenol, the application of  $\text{N}_2\text{O}$  is relatively complex in industrial operation [5]. By comparison, liquid-phase hydroxylation of benzene in the presence of  $\text{H}_2\text{O}_2$  is green and simple, which can be operated under milder reaction conditions, and

ideally water is the only co-product in the process [8]. It should be stressed that phenol itself is more active than benzene; the product is liable to be over-oxidized under oxidative circumstance [6]. In this sense, developing a catalyst that can afford high selectivity and efficient activity is definitely a core topic in the fields of catalytic hydroxylation of benzene.

In the past decade, graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ) has emerged as an appealing metal-free material in multiple fields including heterogeneous catalysis [9–12], photocatalysis [13,14], fuel cells [15,16], and gas adsorbent and storage [17]. In viewpoint of chemical structure,  $g\text{-C}_3\text{N}_4$  is composed by  $\pi$ -conjugated stacking layers, of which tectonic units are heptazine heterocycles bridged by nitrogen atoms [9,18]. Owing to these unique structures,  $g\text{-C}_3\text{N}_4$  shows inherent ability in activating benzene molecule, and has demonstrated potential catalysis in Friedel–Crafts acylation [19] and alkylation [20] reactions, and selective oxidation of benzene [21,22]. Nevertheless, the surface areas of  $g\text{-C}_3\text{N}_4$  materials prepared by direct pyrolysis are very low ( $< 10 \text{ m}^2 \text{ g}^{-1}$ ) [23,24], and meanwhile the catalytic activity of bare  $g\text{-C}_3\text{N}_4$  materials in benzene-activating reactions is indeed limited [19,25]. In this regard, to achieve high catalytic activity, it is desired to increase the surface area and/or introduce other catalytic components featuring oxidative ability.

Han and his coworkers [8] synthesized a series of  $g\text{-C}_3\text{N}_4$ -supported metal oxides (including Ni, Co, Cu, Fe, and V) and found that vanadia

\* Corresponding authors.

E-mail addresses: [shine6832@163.com](mailto:shine6832@163.com) (J. Xu), [xuebing.cn@163.com](mailto:xuebing.cn@163.com) (B. Xue).

catalysts had superior activity to others in hydroxylation of benzene. Very recently, our group [25,26] reported synthesis of mesoporous carbon nitride materials (mp-C<sub>3</sub>N<sub>4</sub>, and CND), which were then applied as catalytic supports to load vanadia, and VO(acac)<sub>2</sub>, respectively. In hydroxylation of benzene to phenol, the supported catalysts exhibited notable catalytic activity. However, it should be pointed out that the mesoporous carbon nitride supports were fabricated by a nanocasting approach using silica as a hard template. The preparation procedure required complicated and time-consuming (basically more than three days including etching and rinsing steps) detemplating step involving volatile and toxic HF or NH<sub>4</sub>HF<sub>2</sub> solution [27,28]. More importantly, in the previous work, the use of mesoporous carbon nitride materials as catalytic supports were actually based on their high surface areas which could well disperse active vanadia. Unfortunately, the influence of chemical environment (especially its nitrogen species) of mesoporous carbon nitride on the loading of vanadia was rarely analyzed.

In view of both green synthesis and manufacturing cost, in the present work, we synthesized mesostructure g-C<sub>3</sub>N<sub>4</sub> materials via exfoliation and protonation, which were thus utilized as catalyst supports to load vanadia for hydroxylation of benzene to phenol. The synthesized supported vanadia catalysts showed superior activity to those catalysts supported on the pristine g-C<sub>3</sub>N<sub>4</sub>, and afforded a maximum yield of phenol as much as 15.2% at 6 h under 60 °C.

## 2. Experimental section

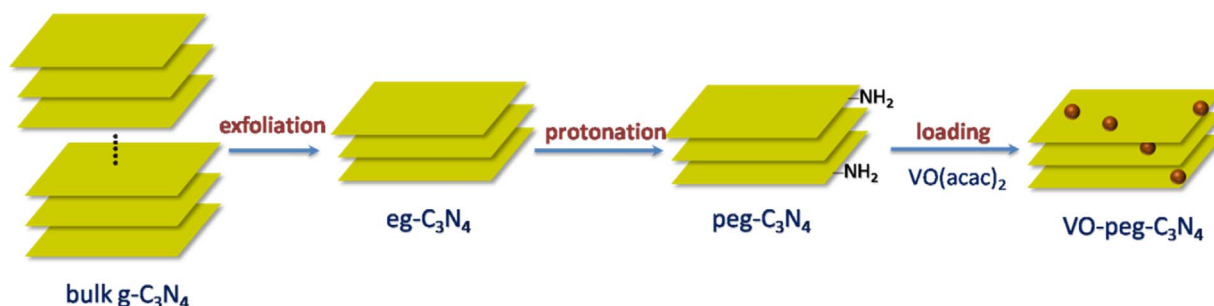
### 2.1. Catalyst synthesis

#### 2.1.1. Synthesis of g-C<sub>3</sub>N<sub>4</sub>, eg-C<sub>3</sub>N<sub>4</sub> and peg-C<sub>3</sub>N<sub>4</sub>

g-C<sub>3</sub>N<sub>4</sub> was synthesized by direct pyrolysis of dicyandiamide (DCDA). Briefly, 4.0 g DCDA was placed in a crucible with a cover, and then statically heated at 550 °C for 4 h. The eg-C<sub>3</sub>N<sub>4</sub> material was prepared by exfoliation of g-C<sub>3</sub>N<sub>4</sub> as follows. 0.5 g of g-C<sub>3</sub>N<sub>4</sub> was further calcinated at 550 °C for 3 h with a ramping rate of 10 °C min<sup>-1</sup>, and the calcination was also conducted in a crucible with a cover. To prepare protonated eg-C<sub>3</sub>N<sub>4</sub>, 0.5 g of eg-C<sub>3</sub>N<sub>4</sub> was treated by 10 mL of HCl solution (a.q.) for 3 h. Next, the mixture was centrifuged and the solid was rinsed by water and finally dried at 80 °C overnight. The protonated eg-C<sub>3</sub>N<sub>4</sub> was labeled as peg-C<sub>3</sub>N<sub>4</sub>-xM, where x indicated the molar concentration of HCl (a.q.). Unless specified, the value was 2 M.

#### 2.1.2. Preparation of VO-peg-C<sub>3</sub>N<sub>4</sub>

0.4 g of peg-C<sub>3</sub>N<sub>4</sub> was added into 30 mL of toluene solution containing 0.1 g of vanadyl(IV) acetylacetonate ([VO(acac)<sub>2</sub>]). The mixture was transferred into a stainless autoclave and charged with N<sub>2</sub> up to 0.7 MPa, and then heated at 80–120 °C for 10 h under vigorous stirring. Afterwards, the dispersion was filtrated and the obtained solid was thoroughly rinsed with toluene. The wet solid was subsequently dried under vacuum at 80 °C for 2 h, and the final product was designated as VO-peg-C<sub>3</sub>N<sub>4</sub>-T, where T was the above heating temperature. Unless specified, the temperature was 120 °C. The overall synthetic procedure from g-C<sub>3</sub>N<sub>4</sub> to VO-peg-C<sub>3</sub>N<sub>4</sub> is illustrated in Scheme 1.



Scheme 1. Synthetic route from g-C<sub>3</sub>N<sub>4</sub> to VO-peg-C<sub>3</sub>N<sub>4</sub>.

### 2.2. Material characterization

Specific Surface areas and porous properties of all the materials were analyzed by nitrogen adsorption–desorption isotherms (–196 °C) tested at using an ASAP 2020 (Micromeritics) instrument. The materials were pretreated by degassing at 150 °C for 6 h. The surface areas were calculated by Brunauer–Emmet–Teller (BET) method; and the pore size distributions were determined according to Barret–Joyner–Halenda (BJH) model using desorption branches. X-ray diffraction (XRD) patterns were recorded on a D/max 2500 (Rigaku) X-ray diffractometer. The analysis used a graphite monochromator (40 kV, 40 mA) coupled with Ni-filtered Cu-K $\alpha$  radiation. Fourier transform infrared (FT-IR) spectra were tested in a Tensor 27 (Bruker) spectrometer based on the transmission mode under room temperature. UV–vis diffuse reflectance spectra (DRS) were carried out on a UV-3600 (Shimadzu) spectrophotometer using BaSO<sub>4</sub> as a standard reference. X-ray photoelectron spectra (XPS) were recorded on a PHI 5000C (Perkin–Elmer) spectrometer working in the constant analyzer energy mode with Mg K $\alpha$  radiation as the excitation source. Thermal gravimetric (TG) measurements were conducted on a TGA 7 (Perkin–Elmer) instrument. All the samples were heated from room temperature to 850 °C at a rate of 20 °C min<sup>-1</sup>, under a flow of N<sub>2</sub> (50 mL min<sup>-1</sup>). Scanning electron microscopy (SEM) was analyzed on a Supra 55 (Zeiss) microscope operating at 30 kV. Transmission electron microscopy (TEM) experiments were carried out on a JEOL 2010 electronic microscope. The content of vanadium was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

### 2.3. Catalytic evaluation

Catalytic hydroxylation of benzene was performed in a round-bottom flask (25 mL). 1 mL of benzene (11.2 mmol), and 6 mL of solvent (5 mL of acetonitrile and 1 mL of acetic acid) were mixed well, followed by addition of 25–75 mg of catalyst. After the mixture was heated up to 60 °C, 3 mL of H<sub>2</sub>O<sub>2</sub> (a.q., 30 wt%) was added into the reactor by a peristaltic pump in 30 min. During the reaction, a small amount of reaction mixture (< 0.15 mL) was collected periodically, centrifuged, and then analyzed by a gas chromatograph (FID with a SE-54 column). The conversion of benzene and selectivity to phenol were calculated by means of an area-normalization method.

## 3. Results and discussions

### 3.1. Characterization results

Firstly, the crystalline structure of g-C<sub>3</sub>N<sub>4</sub>, eg-C<sub>3</sub>N<sub>4</sub>, peg-C<sub>3</sub>N<sub>4</sub>, and VO-peg-C<sub>3</sub>N<sub>4</sub> materials were characterized by XRD (Fig. 1). The pattern pristine g-C<sub>3</sub>N<sub>4</sub> shows an intensive diffraction peak centered at 2 $\theta$  = 27.4°, which corresponds to (002) plane ( $d_{002}$  = 0.325 nm, interlayer stacking structure) of graphitic structure [19]. In addition, a weak peak appearing at 13.1° is indexed as the (100) plane, i.e. intralayer motif of graphitic structure [29]. In the case of other three g-

Download English Version:

<https://daneshyari.com/en/article/6453191>

Download Persian Version:

<https://daneshyari.com/article/6453191>

[Daneshyari.com](https://daneshyari.com)