

# Vapor-Phase Selective Oxidation of Toluene Catalyzed by Graphitic Carbon Nitride Supported Vanadium Oxide

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Abstract Organic materials have seldom been used in vapor-phase reaction due to their poor thermal stability. To solve this problem, toluene vapor-phase oxidation catalyst was fabricated by supporting vanadium oxide onto graphitic carbon nitride  $(g-C_3N_4)$ , an organic material with excellent thermal and oxidative stability. The nitrogen-rich property provides  $g-C_3N_4$  with abundant anchoring sites, leading to high dispersion of vanadium oxide. When used as catalysts for the oxidation of toluene,  $V-g-C_3N_4$  exhibited greatly improved activity and selectivity to benzal-dehyde compared to traditional catalyst. After the vapor-phase reaction at 330 °C for 6 h, no marked deactivation was observed. The TGA, XRD, FT-IR and XPS results revealed that  $V-g-C_3N_4$  keeps constant during this high-temperature process.

### **Graphical Abstract**



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### **1** Introduction

Benzaldehyde has been widely used as versatile intermediates for the synthesis of medicines, dyes, pesticides, solvents, flavors, plastics, preservatives and flame retardants [1, 2]. Commercially, benzaldehyde is produced by the chlorination of toluene followed by saponification. This process is inefficient and the products may be contaminated by chlorine. The direct catalytic side chain oxidation of toluene is a more efficient approach to produce benzaldehyde and has attracted great investigation efforts [3, 4]. Liquidphase oxidation using homogeneous or heterogeneous catalysts has been developed, but the use of organic solvent and the problems related to the separation of products and catalysts limit its application [5–7]. To overcome these problems, vapor-phase oxidation has been considered. Vaporphase oxidation facilitates the continuous operation without the separation of products and catalysts. Many attempts have been made to explore toluene vapor-phase oxidation catalysts. It has been proved that supported vanadium oxide is suitable for the selective oxidation of toluene to benzaldehyde as well as other valuable products [8-10]. Support plays a crucial role in the performance of vanadium based catalyst. To date, TiO<sub>2</sub> [11, 12], ZrO<sub>2</sub> [13], fly ash [14], sepiolite [15] and  $SiO_2$  [16] were employed to support vanadium oxide. However, to avoid over oxidation of toluene to CO<sub>x</sub> and other byproducts, all of the studied catalysts should be operated under controlled conditions and limited conversions. Clearly, there remain numerous challenges in developing efficient catalysts for toluene vapor-phase

oxidation that have greatly improved selectivity while retaining activity.

Currently, the large majority of catalyst supports are inorganic-based. Organic supports are preferred over their inorganic equivalents because they tolerate various functional groups and can be easily functionalized to accommodate different catalytic active species. Thus, organic catalyst supports have attracted significant attention in recent years [17-20]. However, due to the poor thermal stability, organic catalytic materials have seldom been used in vaporphase catalytic reaction which generally performs at relatively high temperature. Graphitic carbon nitride  $(g-C_3N_4)$ , an organic semiconductor, has been widely used as metalfree catalyst or catalyst support in the past decade [21-23]. The thermal and oxidative stability of this material is one of the highest for an organic material. The sublimation or pyrolysis only can occur above 600 °C even in air [24, 25]. In addition,  $g-C_3N_4$  is a nitrogen-rich material. It is composed of tri-s-triazine units connected via trigonal nitrogen atoms. The nitrogen containing groups, such as aromatic amines, primary amines and secondary amines, provide abundant anchoring sites for metal or metallic nanoparticles [26–28]. Based on these properties, we reasoned that g-C<sub>3</sub>N<sub>4</sub> is a suitable organic material for vapor-phase catalytic reactions.

Recently, moderate to excellent results for the liquidphase oxidation of hydrocarbons catalyzed by  $g-C_3N_4$  or  $g-C_3N_4$  supported vanadium oxide have been reported [29–31]. Because both  $g-C_3N_4$  and vanadium oxide can act as the catalytic active sites, it is expected that  $g-C_3N_4$  supported vanadium oxide should be active for the vapor-phase oxidation of the primary C–H bonds in toluene. Herein, we report V–g-C<sub>3</sub>N<sub>4</sub> prepared by an in situ strategy as a significantly improved catalyst for the vapor-phase selective oxidation of toluene.

## 2 Experimental

## 2.1 Materials and Characterization

All chemicals are analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd without further purification. Scanning electron microscopy (SEM) images were recorded on a Hitachi S-4800 instrument. Transmission electron microscopy (TEM) images were obtained on a JEOL JSM-2100 instrument. Nitrogen adsorption–desorption experiment was performed at 77.3 K by a Quantachrome Autosorb Automated Gas Sorption System (Quantachrome Corporation). Before experiments, the samples were dried at 200 °C under vacuum for 6 h. Powder X-ray diffraction (XRD) were performed on a Rigaku Rotaex diffractometer equipped with Cu Kα radiation source (40 kV, 200 mA;  $\lambda = 1.54056$  Å). Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Tensor 27 by using KBr pellets. X-ray photoelectron spectroscopy (XPS) dates were collected on a Thermo Scientic ESCALab 250Xi using 200 W monochromated Al K $\alpha$  radiation. Thermo-gravimetric analysis (TGA) was performed on a Pyris 1 TGA (Perkin Elmer) at a heating rate of 10 °C min<sup>-1</sup> in air flux.

### 2.2 Synthesis of Catalysts

g-C<sub>3</sub>N<sub>4</sub> was synthesized by direct heating 20 g urea at 550 °C for 2 h in still air. The heating rate was 5 °C min<sup>-1</sup>. After cooled to room temperature, g-C<sub>3</sub>N<sub>4</sub> was ground to a homogeneous powder. For the synthesis of V–g-C<sub>3</sub>N<sub>4</sub>, 20 g urea dissolved in 40 mL deionized water was heated and stirred at 100 °C with different amounts of NH<sub>4</sub>VO<sub>3</sub>. The mixed solution was continually heated at this temperature to remove water. The resulting solids were then heated at 350 °C for 2 h in still air with a heating rate of 5 °C min<sup>-1</sup>. After cooled to room temperature, the obtained products were further heated at 550 °C for 2 h under flowing nitrogen atmosphere. The heating rate was 10 °C min<sup>-1</sup>. The final powder was collected and labeled as *x*-V–g-C<sub>3</sub>N<sub>4</sub>, in which *x* represents the mass (in g) of the added NH<sub>4</sub>VO<sub>3</sub>.

 $V/g-C_3N_4$  and  $V/TiO_2$  were synthesized by incipient wet impregnation method. The desired amounts of  $NH_4VO_3$ dissolved in hot deionized water were added to  $g-C_3N_4$  or  $TiO_2$ . The excess water was removed by heating at 100 °C under constant stirring. After dried at 110 °C overnight, the obtained samples were heated in air at 350 °C for 2 h, followed by heating in nitrogen at 550 °C for another 2 h.

### 2.3 Selective Oxidation of Toluene

Toluene selective oxidation were performed in a continuous-flow fixed-bed reactor (10 mm in internal diameter and 400 mm long) at atmospheric pressure. The catalyst (0.5 g) diluted with SiC (150–200 mesh) was pre-treated at the reaction temperature for 30 min in nitrogen flow. Toluene was introduced into a heated evaporator by a syringepump at 1.8 mL h<sup>-1</sup>. The molar ratio of toluene/O<sub>2</sub>/N<sub>2</sub> was 1/9/36. In each test, the reaction reached steady state after 1 h on stream before the tail gas was analyzed by an on-line gas chromatograph equipped with FID and TCD detectors.

#### **3** Results and Discussion

#### 3.1 Characterization of Catalysts

The morphologies of the catalysts were investigated by SEM and TEM (Fig. 1). The SEM image of  $g-C_3N_4$  shows



Fig. 1 a SEM and b TEM images of g-C\_3N\_4. c SEM and d TEM images of 0.3 V–g-C\_3N\_4

a porous structure consisting of many curved nanosheets with lamellar morphology. The average thickness of the nanosheets is about tens of nanometers. A typical layered morphology with obvious mesoporous structures can be observed from TEM image. These mesopores are derived from the partial interconnection and overlapping of the curved nanosheets. No obvious difference between V–g- $C_3N_4$  and g- $C_3N_4$  can be observed, suggesting the introduction of vanadium has little effect on the structure [32–34]. From both SEM and TEM images, vanadium can't be identified from g- $C_3N_4$  clearly, which may be attributed to the homogeneous distribution of vanadium on the support.

The porous structures were further investigated by nitrogen adsorption-desorption experiments. As shown in Fig. 2a and Table 1, the BET specific surface area  $(S_{\text{BET}})$ of 0.3V-g-C<sub>3</sub>N<sub>4</sub> is 51.3 m<sup>2</sup> g<sup>-1</sup>, slightly lower than that of  $g-C_3N_4$  (64.5 m<sup>2</sup> g<sup>-1</sup>). With the increase in vanadium content, both the  $S_{\text{BET}}$  and the pore volume of V-g-C<sub>3</sub>N<sub>4</sub> decrease gradually. g-C<sub>3</sub>N<sub>4</sub> exhibits typical type III isotherms with H3 hysteresis loops locates at  $0.7 < P/P_0 < 1.0$ , indicating the presence of mesopores. The hysteresis loops of V-g-C<sub>3</sub>N<sub>4</sub> starts at the  $P/P_0$  of 0.5, which is much lower than that of  $g-C_3N_4$ . This is caused by the increased mesopores content. As demonstrated by BJH pore size distributions (Fig. 2b), an obvious bimodal pore size distribution is observed for  $g-C_3N_4$ . Compared to  $g-C_3N_4$ , V-g-C<sub>3</sub>N<sub>4</sub> possesses more mesopores (16-25 nm) and less macropores (50-500 nm).

The crystal structures of the samples investigated by XRD are presented in Fig. 3a.  $g-C_3N_4$  shows two



Fig. 2 a Nitrogen adsorption–desorption isotherms and b BJH pore size distribution curves of  $g-C_3N_4$  and  $0.3V-g-C_3N_4$ 

characteristic diffraction peaks at 27.4° and 13.0°, corresponding to the interlayer-stacking structures (002) and in-planar repeating tri-*s*-triazine units (100) respectively [35, 36]. These peaks weaked largely after the introduction of vanadium, suggesting the crystallinity was decreased and more defects were generated. Defects usually act as the active sites for catalytic reactions. The reduced crystallinity lowers the rigidity of V–g-C<sub>3</sub>N<sub>4</sub>,

Table 1 Textural properties of the catalysts

Catalysts	Vanadium content (%)	$S_{\rm BET} ({ m m}^2~{ m g}^{-1})$	Pore volume (cm <sup>3</sup> $g^{-1}$ )	Pore size (nm)	
g-C <sub>3</sub> N <sub>4</sub>	0	64.5	0.46	86.4	
$0.1V - C_3N_4$	3.3	69.5	0.39	54.6	
$0.2V-C_3N_4$	7.43	52.4	0.35	26.8	
$0.3V - C_3N_4$	11.6	51.3	0.33	18.8	
$0.4V - C_3N_4$	15.9	47.8	0.28	16.5	
$0.6V-C_3N_4$	25.8	41.6	0.21	16.1	
V/g-C <sub>3</sub> N <sub>4</sub>	11.3	55.8	0.38	65.8	



Fig. 3 a XRD patterns and b FT-IR spectra of  $g\text{-}C_3N_4$  and  $0.3V\text{-}g\text{-}C_3N_4$ 

resulting in the shrinkage of macropores to mesopores as aforementioned. No signal of vanadium is reflected by XRD, which is in agreement with the SEM and TEM results. FT-IR spectrum of V–g- $C_3N_4$  (Fig. 3b) shows characteristic bands at 812, 1259, 1324, 1423, 1571 and 1632 cm<sup>-1</sup>. This indicates the formation of trigonal nitrogen atoms connected tri-*s*-triazine structure. The condensation of monomers to macromolecules could be inhibited by metals [37, 38]. As a result, both the XRD and FT-IR signals become less pronounced with the increase in vanadium content (Fig. 4).

XPS analysis of V–g-C<sub>3</sub>N<sub>4</sub> confirms the incorporation of vanadium (Fig. 5). Carbon, nitrogen and oxygen are also observed in the survey spectrum. The chemical state of vanadium was further investigated by high resolution V2p XPS spectrum. A binding energy of 516.9 eV for V2p<sub>3/2</sub> is presented (Fig. 5b), which is consistent with the energies characteristic of V<sub>2</sub>O<sub>5</sub> (517.4–516.4 eV). The binding energy of V2p<sub>3/2</sub> is sensitive to the support. 517.0 and 517.1 eV were reported for V<sub>2</sub>O<sub>5</sub> and V<sub>2</sub>O<sub>5</sub>/CeO<sub>2</sub>/SiO<sub>2</sub>



Fig. 4 a XRD patterns and b FT-IR spectra of of V-g- $C_3N_4$  with different vanadium contents

respectively [39, 40]. The slightly lowed binding energy of  $V2p_{3/2}$  for V–g-C<sub>3</sub>N<sub>4</sub> may be attributed to the interaction of vanadium with nitrogen, which leads to an increased electron cloud density of vanadium.

#### 3.2 Selective Oxidation of Toluene

The vapor-phase oxidation of toluene were carried out in a fixed-bed reactor. Benzaldehyde, benzoic acid and  $CO_x$ were found to be the main products. Heavier oxidized products, such as maleic anhydride, phthalic anhydride and some coupling products were also detected. Table 2 lists the experimental results for various catalysts. V/TiO<sub>2</sub>, the most widely reported catalyst for the vapor-phase oxidation of toluene, was investigated for comparison. A selectivity of 29.4% to benzaldehyde at the conversion of 2.8% was obtained. No detectable product can be found when bare g-C<sub>3</sub>N<sub>4</sub> was used as the catalyst in our experiments, although mesoporous g-C<sub>3</sub>N<sub>4</sub> was reported to be able to activate molecular oxygen [29]. The catalytic activity



Fig. 5 a XPS survey spectrum and b V2p spectrum of 0.3V–g-C<sub>3</sub>N<sub>4</sub>

increased abruptly when vanadium was incorporated into  $g-C_3N_4$ , suggesting vanadium oxide is the catalytic active site.  $0.1V-g-C_3N_4$  gave a conversion of 3.8%. Compared to V/TiO<sub>2</sub>, the selectivity to benzaldehyde increased largely to 67.8%. The enhanced catalytic performance is possibly due

to the improved dispersion of vanadium. As demonstrated by the V2p XPS spectrum (Fig. 2d), vanadium may interact with the nitrogen containing groups in g-C<sub>3</sub>N<sub>4</sub>. As a result, vanadium can be supported onto  $g-C_3N_4$  homogenously, resulting in vanadia species with enhanced catalytic performance [41-43]. The vanadium content affects the catalytic performance significantly. The conversion increased to 6.2 and 7.1% for 0.2V-g-C<sub>3</sub>N<sub>4</sub> and 0.3V-g-C<sub>3</sub>N<sub>4</sub> respectively. Further increase in the vanadium content, a negative effect was observed. The conversion decreased slightly to 6.9% for  $0.4V-g-C_3N_4$  and 5.3% for  $0.6V-g-C_3N_4$ . The deteriorated performances of these catalysts may be caused by the deformed porous structures and decreased  $S_{\text{BET}}$  (Table 1). It is clear that the selectivity to benzaldehyde decreases significantly with the increase in vanadium content. At low vanadium content, vanadium oxide spreads over the  $g-C_3N_4$ surface homogenously due to the interaction of vanadium and the nitrogen atoms in  $g-C_3N_4$ . Upon increasing the vanadium loading, crystalline vanadia species are developed, resulting in the over oxidation of benzaldehyde. The preparation method plays a crucial role in the performance of the catalysts.  $V/g-C_3N_4$  prepared by wet impregnation shows poor vanadium dispersion than  $V-g-C_3N_4$  prepared by in situ method. As a result, the activity and selectivity of V/g-C<sub>3</sub>N<sub>4</sub> decreased significantly compared to that of  $V-g-C_3N_4$ .

### 3.3 The Stability of the Catalysts

To investigate the stability of V–g- $C_3N_4$ , the TGA were performed. Generally, g- $C_3N_4$  exhibits excellent thermal stability. The thermal decomposition and vaporization only starts at 630 °C in air [24, 25]. Therefore, g- $C_3N_4$ is an ideal organic material that can be used in vaporphase reactions at high temperature. However, as demonstrated by Fig. 6, an obvious weight loss starts at approximately 365 °C for 0.3V–g- $C_3N_4$ . This can be attributed

Entry	Catalyst	Con. (%)	Selectivity (%)			
			BA <sup>a</sup>	BAc <sup>b</sup>	CO <sub>x</sub>	Others
1	V/TiO <sub>2</sub>	2.8	29.4	21.6	17.5	31.5
2	$g-C_3N_4$	0	-	_	-	-
3	$0.1V$ –g- $C_3N_4$	3.8	67.8	7.6	6.3	18.3
4	$0.2V-g-C_3N_4$	6.2	46.6	19.5	18.7	15.2
5	$0.3V-g-C_3N_4$	7.1	43.2	23.6	19.9	13.3
6	$0.4V-g-C_3N_4$	6.9	29.6	31.4	23.6	15.4
7	$0.6V-g-C_3N_4$	5.3	21.8	28.7	29.4	20.1
8	V/g-C <sub>3</sub> N <sub>4</sub>	2.5	31.6	22.8	25.4	20.2

Table 2Vapor-phase oxidationof toluene over various catalysts

Reaction conditions: catalyst (0.5 g), toluene (1.8 ml min<sup>-1</sup>), toluene/ $O_2/N_2$  (1/9/36), temperature (330 °C) <sup>b</sup>Benzaldehyde

<sup>c</sup>Benzoic acid



Fig. 6 TGA curve of 0.3V–g-C<sub>3</sub>N<sub>4</sub> at a heating rate of 10 °C min<sup>-1</sup> under air flux

to the oxidation of  $g-C_3N_4$  by air. A similar result has been reported for Fe–C<sub>3</sub>N<sub>4</sub>, which showed 60% weight loss after calcination in air at 400 °C [44]. The catalytic capacities of vanadium and iron are the main reasons for the sharply decreased oxidation temperature of  $g-C_3N_4$ .

The conversion and selectivity to benzaldehyde and benzoic acid as a function of temperature are presented in Fig. 7. The conversion increased largely from 0.6 to 7.1% when the temperature was raised from 290 to  $330 \,^{\circ}$ C, and maintained at this level at  $350 \,^{\circ}$ C. This means that the catalyst is stable during the vapor-phase reaction at  $350 \,^{\circ}$ C. Further increase in the temperature to  $370 \,^{\circ}$ C, the conversion decreased sharply to 0.2%. This is caused by the decomposition of the support. With the increase in the temperature, more benzaldehyde was oxidized to benzoic acid. As a result, the selectivity to benzaldehyde decreased while the selectivity to benzoic acid increased. When the temperature is higher than  $350 \,^{\circ}$ C,



Fig. 7 Effects of reaction temperature on the oxidation of toluene catalyzed by  $0.3V\mathac{-}g\mathchar{-}C_3N_4$ 

deep oxidation products such as  $CO_x$  increased via the oxidation of benzoic acid, resulting in the decrease in the selectivity to benzoic acid.

To further examine the stability of the catalyst, the reaction profile at 330 °C over an initial 6-hour reaction period was investigated. As presented in Fig. 8, both the conversion of toluene and the selectivity to benzaldehyde and benzoic acid have not changed significantly within 6 h. The conversion dropped from 7.1 to 6.8% and the selectivity to benzaldehyde decreased from 43.2 to 38.4%, while the selectivity to benzoic acid increased from 23.6 to 26.1%. This indicates that the investigated catalyst exhibits excellent stability at 330 °C.

The crystal structures of the used catalysts were investigated by XRD (Fig. 9a). After vapor-phase reaction at 330 °C for 6 h, both the (100) and (002) peaks have not changed obviously, suggesting the catalyst is stable under this temperature. However, when the temperature was raised to 350 °C, the destruction of g-C<sub>3</sub>N<sub>4</sub> was revealed by the weakened and broadened XRD peaks. It was demonstrated by TGA that V-g-C<sub>3</sub>N<sub>4</sub> starts to be oxidized at 365 °C. We ascribe the decreased decomposition temperature during vapor-phase oxidation to the temperature gradient and hot spots in the fixed-bed reactor. The FT-IR experiments show a similar result (Fig. 9b). There is no obvious difference between the FT-IR spectra of V-g-C<sub>3</sub>N<sub>4</sub> before and after reaction at 330 °C. But the FT-IR signals of the catalyst after reaction at 350 °C weakened largely due to the destruction of the support.

The chemical state of V–g-C<sub>3</sub>N<sub>4</sub> before and after reaction at 330 °C was investigated by XPS experiments. As shown in Fig. 10a, three chemical states of nitrogen at 398.6, 399.5 and 400.8 eV, corresponding to C–N=C (N1), N–(C)<sub>3</sub> (N2), and NH/NH<sub>2</sub> (N3) respectively, can be fitted from N1s XPS spectra. The percentage of each chemical state were summarized in Table 3. It is clear that the



Fig. 8 Effects of reaction time on the oxidation of toluene catalyzed by  $0.3V\mbox{-g-}C_3N_4$ 



Fig. 9 a XRD patterns and b FT-IR spectra of 0.3V–g-C<sub>3</sub>N<sub>4</sub> before and after reactions at 330 and 350 °C

contents of N1, N2 and N3 have no marked fluctuations after the reaction. This demonstrates that the core structure of  $g-C_3N_4$  keeps constant during the vapor-phase catalytic process. The chemical state of carbon changed significantly after the reaction. The C1s XPS spectra were fitted into two peaks at 284.8 and 288.4 eV, corresponding to graphitic carbon and carbon in tri-*s*-triazine, respectively [45, 46]. After the reaction, the graphitic carbon increased greatly from 16.7 to 61.9%. The increased graphitic carbon is probably ascribed to toluene and its oxidation products. These carbon-containing substances can be strongly adsorbed on the surface of the catalysts and can't be removed even under vacuum conditions [16]. The coverage of active sites with these substances may resulted in the slightly decrease in the catalytic activity as aforementioned.

## 4 Conclusions

To conclude,  $g-C_3N_4$  supported vanadium oxide catalysts have been developed for the vapor-phase oxidation of toluene. For this high temperature reaction,  $g-C_3N_4$  shows distinct advantages over traditional organic supports due



Fig. 10 N1s and C1s XPS spectra of 0.3V–g-C\_3N\_4 before and after reactions at 330  $^\circ\text{C}$ 

**Table 3** Percentage of each chemical state of nitrogen and carbon in 0.3V-g-C<sub>3</sub>N<sub>4</sub> before and after reaction at 330 °C

	N1 (%)	N2 (%)	N3 (%)	C1 (%)	C2 (%)
Before	52.0	28.3	19.7	16.7	83.3
After-330	53.7	25.1	21.2	61.9	38.1

to its extremely high thermal stability. Despite the largely decreased pyrolysis temperature due to the catalytic capacity of vanadium, g-C<sub>3</sub>N<sub>4</sub> keeps constant during the vapor-phase catalytic reaction at 330 °C. The nitrogenrich property provides  $g-C_3N_4$  with abundant anchoring sites, leading to high dispersion of vanadium oxide. Compared to the reported V/TiO<sub>2</sub> catalyst, V–g-C<sub>3</sub>N<sub>4</sub> exhibits greatly improved selectivity while retaining high activity. Herein, vapor-phase selective oxidation of hydrocarbon using organic material supported metal catalysts is achieved.

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