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Noble metal free $V_2O_5/g-C_3N_4$ composite for selective oxidation of olefins using hydrogen peroxide as oxidant

Hui Zou,^a Guansheng Xiao,^a Kaihao Chen^a and Xinhua Peng*^a

Vanadium pentoxide modified graphitic carbon nitride ($V_2O_5/g-C_3N_4$) composites were prepared through a method of wet impregnation and calcination. The obtained samples were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, thermogravimetric analysis, X-ray photoelectron spectroscopy, scanning electron microscope, transmission electron microscopy, UV-vis diffuse reflectance spectroscopy, photoluminescence, electron spin resonance and N_2 adsorption/desorption isotherms. The oxidation of olefins was employed to evaluate the catalytic and photocatalytic activity of the prepared $V_2O_5/g-C_3N_4$ composites. Different weight ratios (1%, 2%, 3%, 4% and 5%) of V_2O_5 loaded composites were prepared and a 3% loaded composite was found to show optimal catalytic performance for the reaction. This noble metal free catalyst showed excellent performance in the oxidation of styrene to benzaldehyde with high conversion (98.7%) and selectivity (88.4%) under visible light irraiation. A plausible mechanism was proposed for this oxidation reaction with hydrogen peroxide as oxidant. Other styrene substrates were also selectively transformed to the corresponding aldehydes with high yield (up to 92%), using such noble metal free catalytic system.

1. Introduction

The partial oxidation of olefins to the corresponding aldehydes is significant in organic synthesis and industrial chemistry.^{1, 2} In the past several decades, tremendous efforts have been devoted to achieving this transformation based on homogenous catalysts, such as metalloporphyrins, transition metal-schiff bases and metal-phthalocyanines.³⁻⁵ However, the majority of these catalysts are suffering from difficulties in separation from the reaction mixture and generating copious waste. In addition, most of these homogenous catalysts become inactive after reaction, which is not desirable in industrial application.⁶

To circumvent these problems, heterogeneous catalysts have been successfully developed for the oxidation of olefins.⁷⁻¹⁰ The common strategy is to anchor active sites on various solid support, such as molecular sieve, graphene oxide, reduced graphene oxide and clay.¹¹⁻¹⁵ Most of the reported catalysts for such oxidation involve noble metals, for example, gold, silver, palladium, platinum etc.^{7,16-18} Unfortunately, they are usually expensive, tedious and environmentally unfriendly. The above disadvantages may hamper their practical application in industries. Therefore, it's imperative to explore some new heterogeneous catalysts which are simple, environmentally friendly, inexpensive and recyclable.

Recently, graphitic carbon nitride $(g-C_3N_4)$ has drawn considerable attention in the field of catalysis and became a continuous hot topic in both academic research and industrial

application.¹⁹⁻²³ The g-C₃N₄ materials exhibit excellent performance as promising catalysts due to the similarity to graphene, high chemical, thermal stability and easily tailorable structure.²⁴ Graphitic carbon nitride is widely used in oxidation,²⁵ photocatalysis²⁶ and photodegradation of pollutants.²⁷ Thus far, many g-C₃N₄ based catalysts have been reported to apply in the oxidation of olefins. Most of the reported g-C₃N₄ catalysts are employed to catalyse the substrates to relevant ketones or epoxides with low conversion and selectivity.²⁸⁻³⁰ Few researches focus on the transformation of olefins to the corresponding aldehydes.

Herein, we have prepared vanadium pentoxide (V₂O₅) supported on g-C₃N₄ by a mild wet impregnation and calcination method with ammonium metavanadate (NH₄VO₃) and melamine as precursors. The as-prepared V₂O₅/g-C₃N₄ catalysts are firstly employed to the selective oxidation of olefins.

2. Experimental

2.1 Sample preparation

Vanadium pentoxide was prepared using NH₄VO₃ as precursor. In detail, 1.17 g NH₄VO₃ and 5.76 g citric acid were dissolved in deionized water and the resulting mixture was stirred at ambient condition for 30 min. The obtained solution was heated to 100 °C to remove water. The residue remained was calcined at 500 °C for 2 h with ramping rate of 5 °C/min to prepare pure V₂O₅.

Graphitic carbon nitride was synthesized via thermal polycondensation of melamine according to the previous report.¹⁹ Typically, 10 g melamine was put into an alumina crucible with cover to avoid the sublimation of precursor, then heated to 550 $^{\circ}$ C under air atmosphere with a rate of 10 $^{\circ}$ C/min and kept at this

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temperature for 4 h in a muffle furnace. After cooling to room temperature, the obtained yellow product was ground into powder for further use.

The $V_2O_5/g-C_3N_4$ composite catalysts with different amounts of V_2O_5 were prepared according to the following process: 0.2 g bulk $g-C_3N_4$ with different weight ratios of V_2O_5 (1%, 2%, 3%, 4% and 5%) were added into 20 mL methanol, respectively. Then the ensuing mixture was treated with ultrasonic for 30 min. Immediately after the sonication, the resulting suspension was vigorously stirred at 80 °C to evaporate methanol. Then the remaining product was annealed in a muffle furnace at 400 °C for 2 h with a heating rate of 5 °C/min. To be clear, the obtained catalysts with expected different weight ratios of V2O5 (1%, 2%, 3%, 4% and 5%) were collected as VC-1, VC-2, VC-3, VC-4 and VC-5, respectively. Bare V_2O_5 and $g-C_3N_4$ were studied with the same procedure for comparison.

2.2 Characterization

Fourier transform infrared (FT-IR) spectra were recorded on a NicoletIS-10 spectrometer using KBr as the reference. The structures of those prepared samples were analysed by a Bruker D8 Advance diffractometer with Cu K radiation (λ = 1.5406 Å). TG analysis was performed on TGA/SDTA851 with a ramping rate of 10 °C/min under air atmosphere. XPS data was collected on a PHIQuantera II instrument with Al K α as X-ray source. A scanning electron microscopy (SEM) S-4800 was employed to examine the morphology of the samples. The TEM images were also obtained using a Tecnai 12 transmission electron microscope. UV-visible diffuse reflectance spectra of the samples were studied by a ThermoFisher Evolution 220 UV-vis spectrophotometer. The photoluminescence (PL) measurements were carried out on a FL3-TCSPC at room temperature. The electron spin resonance (ESR) analysis was conducted with a JES-FA200 spectrometer. The N₂ adsorption/desorption isotherms were obtained at 77 K using an Autosorb IQ3 instrument. The high-resolution transmission electron microscopy (HRTEM) image was obtained using a JEM-2100 transmission electron microscope.

2.3 Oxidation of olefins

In a 50 mL two-necked round bottomed flask, olefin (1 mmol), catalyst VC-3 (20 mg), and 5 mL of acetonitrile were added together. After admixing, 30wt% H₂O₂ (6 mmol) was added into the above mixture and the system was refluxed at 70 $^{\circ}\mathrm{C}$ with continuous stirring, along with simultaneous irradiation using 36 watt domestic bulb. Reaction was performed under the same conditions without visible light irradiation. TLC was used to monitor the progress of reaction until the substrate was completely transformed. Then the catalyst was separated by centrifuge and products were extracted with ethyl acetate. After drying over sodium sulfate, products were analysed by gas chromatography (GC).

3. Results and discussion.

Fig. 1 shows the FT-IR spectra of the as-prepared $g-C_3N_4$, V_2O_5 and $V_2O_5/g-C_3N_4$ composites. In the spectrum of $g-C_3N_4$, characteristic band at 804 cm⁻¹ is attributed to out-of plane bending models of C-N heterocycles.³¹ Peaks at 1245, 1328, 1407, 1573 and 1637 cm⁻¹ are associated with the stretching

vibration of C=N and aromatic C–N heterocycles.³² Three strong absorption bands at 612, 827 and 1019 cm⁻¹ are detected in the V_2O_5 sample, the bands at 612 and 827 cm⁻¹ are assigned to asymmetric stretching modes of the V-O-V bond, and the other band at 1019 cm⁻¹ is associated with the stretching vibration of the V=O bond.³³ As for the spectra of g- C_3N_4 based catalysts, typical bands of at 1200 to 1700 cm⁻¹ and the triazine units at 804 cm⁻¹ are discernible in $V_2O_5/g-C_3N_4$



composites.³⁴ This demonstrates that the loading of V_2O_5 doesn't change the structure of g-C₃N₄, which is also confirmed by XRD analysis.

Fig. 1 FT-IR spectra of g-C₃N₄, VC-1, VC-2, VC-3, VC-4, VC-5 and V₂O₅ samples.

The XRD patterns of the as-prepared g-C₃N₄, V₂O₅ and $V_2O_5/g-C_3N_4$ samples are displayed in Fig. 2. The two distinct diffraction peaks of bulk $g-C_3N_4$ at 13.0° and 27.5° are attributed to the (100) and (002) planes of graphite-like carbon nitride, respectively.³⁵ All the characteristic peaks detected in the pattern of V_2O_5 can be assigned to the orthorhombic V_2O_5 (JCPDS 65-0131),³⁶ which reveals the excellent crystalline of synthesized V_2O_5 . For the V_2O_5/g - C_3N_4 composites, both the distinct diffraction peaks of g-C₃N₄ and the orthorhombic phase of V₂O₅ can be clearly observed and no other impurity is found. In addition, the peak intensities of g-C₃N₄ decrease gradually, while the characteristic peaks of V2O5 become increasingly distinct with the increasing loading of V₂O₅. The



Fig. 2 XRD patterns of g-C₃N₄, VC-1, VC-2, VC-3, VC-4, VC-5 and V₂O₅ samples.

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Thermogravimetric (TG) analysis of V_2O_5 , $g-C_3N_4$ and $V_2O_5/g C_3N_4$ composites are displayed in Fig. 3. As can be seen, pure V_2O_5 exhibits negligible mass loss even heated to 900 °C, while pure $g-C_3N_4$ and $V_2O_5/g-C_3N_4$ samples show significant weight loss at the same temperature. For pure g-C₃N₄, the weight loss is occurred at approximately 600 $^{\circ}$ C and it shows an entire weight loss at roughly 700 °C. As for the prepared $V_2O_5/g-C_3N_4$ composites with increasing amount of V₂O₅, the beginning temperature of the mass loss is lower than pure g-C₃N₄. The weight loss of g-C₃N₄ based materials is mainly attribute to the thermal decomposition of g-C₃N₄ and the remained residue is associated with the content of V_2O_5 . The loss of weight is 98.6%, 98.1%, 96.5%, 96.1% and 95.4%, respectively, which is similar to the expected amount of V_2O_5 .



Fig. 3 TG analysis of g-C₃N₄, VC-1, VC-2, VC-3, VC-4, VC-5 and V₂O₅ samples.



na na nu sao Binding energy (eV) Fig. 4 XPS spectra of VC-3 sample.

XPS measurement was employed to investigate the surface compositions and chemical states of the as-prepared VC-3 sample. Fig. 4 shows the XPS spectrum of VC-3 sample and high-resolution spectra of C 1s, N 1s, V 2p and O 1s. In the spectrum of C 1s, the binding energy at 284.8 eV was selected as the reference for calibration. The strong peak at 288.2 eV of C 1s spectrum is attributed to the N-C-N coordination in $g-C_3N_4$. In the N 1s spectrum, peak at 398.7 eV is associated with the sp² hybridization of nitrogen atoms (C=N-C). As for the spectrum of V 2p, two peaks at 524.5 and 517.0 eV are detected, which are assigned to V 2p1/2 and V 2p3/2 levels, respectively. An obvious peak centered at 532.5 eV is found in the spectrum of O 1s, which corresponds to the oxygen atom in V_2O_5 . The above results convince the presence of V_2O_5 and g-C₃N₄ in the VC-3 sample.

The morphologies of $g-C_3N_4$ and VC-3 sample were



investigated by scanning electron microscope (SEM). As shown in Fig. 5, pure g-C₃N₄ exhibits obvious stacked-up flakes with rough surface. In the case of the VC-3 sample, there is no visible difference between g-C₃N₄ and VC-3 sample, which indicates that the loading of V_2O_5 doesn't change the morphology of $g-C_3N_4$.

Fig. 5 SEM images of (a) $g-C_3N_4$ and (b) VC-3 samples.

Transmission electron microscopy (TEM) was used to further analyse the morphologies and microstructures of $g-C_3N_4$ and VC-3 sample. It's clearly seen from Fig. 6 that pure $g-C_3N_4$ appears a nanosheet like structure. As for VC-3 sample, it can be seen that a few small V₂O₅ nanoparticles are wrapped by the thin layers of $g-C_3N_4$.



Fig. 6 TEM images of (a) $g-C_3N_4$ and (b) VC-3 sample. The HRTEM image in Fig. 7 shows the lattice spaces of VC-3 sample. The lattice fringe spacing is 0.289 nm, which belongs to the (301) planes of V_2O_5 .



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Fig. 7 HRTEM image of VC-3 sample.

Fig. 8 shows the N₂ adsorption-desorption isotherms and the BJH pore size distribution curves of g-C₃N₄ and VC-3 samples. Both samples exhibit type IV adsorption isotherm, indicating the presence of mesopores. The BET surface area of g-C₃N₄ and VC-3 samples are 28.7 and 56.9 m² g⁻¹, respectively. In addition, the pore size distribution curves of both samples show a range of pore diameter from 2 to 16 nm.



Fig. 8 (a) N_2 adsorption–desorption isotherms for $g\text{-}C_3N_4$ and VC-3 samples; (b) pore size distribution for $g\text{-}C_3N_4$ and VC-3 samples.

The UV-vis diffuse reflectance spectra of V_2O_5 , g-C₃N₄ and $V_2O_5/g-C_3N_4$ composites are shown in Fig. 9. As can be seen in the Fig. 9 (a), the absorption edge of $g-C_3N_4$ is around 460 nm while V₂O₅ exhibits an absorption edge at 580 nm. As for V2O5/g-C3N4 composites, obvious red-shifts are observed among these materials compared with pure g-C₃N₄. The results imply that the loading of V_2O_5 on $g-C_3N_4$ can highly broaden the absorption edge of g-C₃N₄ based materials. No distinct difference in photoabsorption performance is discovered among the above $V_2O_5/g-C_3N_4$ samples with different amounts of V_2O_5 . In addition, the band gap energy of the as-prepared materials can be calculated according to the following formula: $(hv-E_a)^{n/2}$ αhv Α (1)

where α , h, v, E_g and A are absorption coefficient, Planck constant, light frequency, band gap energy and a constant, respectively. Besides, the value of n is different with different types of optical transition of a semiconductor (n = 1 for direct transition and n = 4 for indirect transition). The band gap

energy of g-C₃N₄ and V₂O₅ are obtained from the plots of $(\alpha hv)^{1/2}$ vs. hv and $(\alpha hv)^2$ vs. hv, respectively.³⁷ As shown in Fig. 9(b), the band gap energy of g-C₃N₄ is estimated to be 2.61 eV and V₂O₅ is found to be 2.21eV, which are similar to the previous reports.^{38,39} Furthermore, the band gap energy of g-C₃N₄ based composites is estimated to be 2.56, 2.31, 2.29, 2.26 and 2.23 eV, respectively.

Fig. 9 (a) UV–vis diffuse reflection spectra of as-prepared samples; (b) Plots of the $(\alpha hv)^{1/2}$ vs. hv for g-C₃N₄ and other g-C₃N₄ based samples, plots of the $(\alpha hv)^2$ vs. hv for V₂O₅.

The photoluminescence measurement was employed to estimate the efficiency of charge carriers separation and transfer ability of the as-prepared samples. Fig. 10 describes the PL spectra of $g-C_3N_4$ and $V_2O_5/g-C_3N_4$ composites under 390 nm excitation at 25 °C. It's well known that the lower PL intensity has inherent affinity for the slow recombination of charge carriers, which may be favourable for improving the photocatalytic performance.⁴⁰ A broad visible emission peak centered at around 460 nm is detected for pure $g-C_3N_4$. After loading V_2O_5 , the PL intensity of $V_2O_5/g-C_3N_4$ samples decreases rapidly, implying that the recombination rate of charge carriers is much lower compared with pure $g-C_3N_4$. This is beneficial for the enhancement of photocatalytic process.



Fig. 10 PL spectra of $g-C_3N_4$, VC-1, VC-2, VC-3, VC-4 and VC-5 samples.



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Transition metals such as vanadium, cobalt and molybdenum, have gained a lot of attention as catalysts for

Entry	Catalyst	hv	Time	Con.	Sel. (%) ^b			
			(h)	(%) ^b	BzA ^c	PhED ^d	BzAc ^e	
1^{f}	$g-C_3N_4$	+	24	19.2	31.3	trace	trace	
2 ^{<i>g</i>}	$g-C_3N_4$	-	24	10.4	21.5	trace	trace	
3	VC-1	+	1	38.4	92.7	3.80	3.50	
4	VC-2	+	1	89.5	87.6	4.90	7.50	
5	VC-3	+	1	98.7	88.4	4.50	7.10	
6	VC-4	+	1	98.8	82.6	5.30	12.1	
7	VC-5	+	1	99.4	78.4	4.40	17.2	
8	V ₂ O ₅	+	6	72.4	76.7	1.60	21.7	
9	V_2O_5	-	6	71.5	74.2	2.40	23.4	
10	VC-3	-	1	77.5	86.8	2.50	10.7	
11^{h}	VC-3	+	1	53.7	89.4	4.80	5.80	
12 ⁱ	VC-3	+	1	99.3	85.4	4.00	10.6	
13 ^{<i>i</i>}	VC-3	+	1	99.1	82.6	4.10	13.3	
^{<i>a</i>} Reaction conditions: styrene (1 mmol), acetonitrile (5 mL),								
catalyst (20 mg), H_2O_2 (6 mmol), 70 °C. ^b Determined by GC. ^c								
Benzaldehyde. ^d Phenyl-1,2-ethanediol. ^e Benzoic acid. ^f The								
selectivity of styrene oxide was 68.7%. ^g The selectivity of styrene								
oxide was 78.5%. ^h Catalyst (10 mg). ⁱ Catalyst (30 mg). ^j Catalyst								
(40 mg).								

reactions.⁴¹⁻⁴⁴ Especially, the oxidation vanadium widespreadly applied in the oxidation of olefins with excellent catalytic performance.⁴⁵⁻⁴⁷ It inspires us to exam the possibility of combing V_2O_5 with g-C₃N₄, which will highly facilitate the oxidation process. The next crucial step is to find the appropriate ratio of V_2O_5 loading that is optimum for the oxidation reaction. Different amounts of $V_2 O_5 \, \text{were loaded on}$ the surface of $g-C_3N_4$ by a mild method of wet-impregnation and calcination. Here, the catalytic activity of g-C₃N₄ based catalysts was examined in the selective oxidation of styrene using H₂O₂ as co-oxidant and results are summarized in Table 1. The major products of the transformation are benzaldehyde, phenyl-1, 2-ethanediol and benzoic acid. As shown in the table, the weight ratio of V_2O_5 is important for the transformation of styrene to benzaldehyde. Without loading V_2O_5 , the conversion of styrene is very low either in the dark or under visible light (entries 1, 2). Owing to these results, it can be speculated that pure $g-C_3N_4$ is not active enough to catalyse the oxidation of styrene. The conversion of styrene increases to 38.4% with 92.7% selectivity of benzaldehyde using VC-1 as catalyst (entry 3). The increase weight ratio of V₂O₅ loading to 2% rapidly improves the conversion to 89.5% along with benzaldehyde selectivity of 87.6% (entry 4). It's worth noting that styrene was completely transformed under visible light and the selectivity of benzaldehyde reached 88.4% when the amount of V₂O₅ increased to 3% (entry 5). However, no positive effect on the reaction is detected with the further increase amount of V_2O_5 , there is an evident decline in the selectivity of benzaldehyde accompanied by the increase amount of benzoic (entries 6, 7). This can be attributed to the excessive oxidation of styrene to corresponding carboxylic acid. A control experiment was carried out under similar condition using pure V_2O_5 as catalyst, the conversion of styrene and the selectivity

of benzaldehyde is 72.4% and 76.7% (entry 8), respectively. The results indicate that independent V_2O_5 or $g-C_3N_4$ cannot effectively promote the transformation of styrene into benzaldehyde. It's the combination of V_2O_5 and $g-C_3N_4$ that rapidly increases the activity of the catalyst and the affinity of $g-C_3N_4$ toward visible light also has a positive impact on the reaction. There is little difference when bulk V_2O_5 is employed in such reaction under visible-light irradiation compared with the reaction carried out in dark (entries 8,



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9). The enhanced catalytic performance of the catalyst is possibly due to the synergic effect between V_2O_5 and $g-C_3N_4$. After confirming the optimal loading of V_2O_5 , it's necessary to determine the optimum amount of catalyst. Therefore, a series of experiments were performed using 10 mg, 20 mg, 30 mg and 40 mg of catalyst. Styrene is not entirely transformed when 10 mg of catalyst is applied to the reaction (entry 11). 20 mg of VC-3 catalyst is found to possess the most outstanding activity in the oxidation of styrene as it affords 98.7% conversion of styrene and 88.4% selectivity of benzaldehyde. Further increase in the weight of catalyst does not show any significant change in the conversion and selectivity (entries 12, 13).

Table 1 Catalytic performance of prepared samples for the oxidation of styrene with (+) and without (-) visible light^{*a*}

It's well recognized that the \cdot OH radical obtained from the decomposition of H₂O₂, has a strong ability to oxidize substrates into desired products.⁴⁸⁻⁵⁰ For the present reaction system, in order to investigate whether the \cdot OH is involved in the reaction process, 10 mol% isopropanol (a well-known \cdot OH scavenger) was added into the reaction under optimal condition, and the conversion of styrene decreased a lot.



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These results demonstrates that the oxidation reaction is possibly carried out through the •OH radical pathway. The electron spin resonance (ESR) and DMPO (5, 5-dimethyl-1pyrroline N-oxide) spin trap technique were used to further confirm the presence of •OH radicals. As shown in the Fig. 11, the four characteristic peaks of the DPMO-•OH adducts with the relative intensity ratio of 1:2:2:1 are observed. It indicates that •OH radicals are produced in current catalytic system.

Fig. 11 DMPO spin-trapping ESR spectrum for DMPO-•OH under visible light irradiation with VC-3 catalyst.

Based on the above results and discussions, a plausible mechanism for the selective oxidation of styrene to benzaldehyde is proposed as followings:

As illustrated in Fig. 12, under visible light irradiation, both $g-C_3N_4$ and V_2O_5 can be excited to generate electron-hole pairs. After loading V_2O_5 particles, the probability of electron-hole recombination decreases sharply which is confirmed by the PL analysis (Fig. 10). The photogenerated electrons in the conduction band (CB) of $g-C_3N_4$ tend to transform to V_2O_5 , while the holes in the valence band (VB) of V_2O_5 have the opposite transform tendency. And then, H_2O_2 molecules can be decomposed into active oxygen species (•OH) in the presence of $V_2O_5/g-C_3N_4$ composite. The obtained •OH radicals will react with styrene and form radical **A**. Immediately, radical **A** is further combined with the radical •OH and generates the intermediate 1-phenyl-1, 2-ethanediol. Finally, benzaldehyde is prepared from 1-Phenyl-1, 2-ethanediol.

Fig. 12 A plausible mechanism for the reaction.

The recyclability of catalyst is an important parameter to evaluate the performance of catalytic system. Therefore, a series of experiments were performed for the selective oxidation of styrene using VC-3 as catalyst under optimal conditions. After reaction, catalyst was separated from the mixture by centrifugation, washed with ethanol and deionized water, then dried at 70 °C overnight before applying to a new reaction. It can be seen from the results in Fig. 13a that VC-3 can be reused for seven times without obvious decrease of activity. The XRD pattern of VC-3 catalyst after seventh cycle shows little difference compared with the fresh one (Fig. 13b).



Fig. 13 (a) Recycle of catalyst; (b) XRD patterns of VC-3 sample: fresh and after seventh cycle.

The oxidation of a wide range of substituted styrene as well as relevant aromatic olefins was carried out under optimal conditions and results are summarized in Table 2. It can be seen from the results that the position of substituted groups (*meta* and *para*) does not show any significant difference in

the conversion and selectivity (entries 2, 4). However,	the								
conversion of substrate decreases dramatically when	the								
substituent group is at ortho-position (entry 3). It is worth									
Table 2 Extension of substrates ^a									

Entry	Substrate	Product	Time	Yield ^b
			(h)	(%)
1			1	87
2			1	80
3			2.5	46
4			1.5	78
5			1.5	83
6			2	76
7			1	88
8			1	89
9			12	43
10			12	25
11			12	trace

 a Reaction conditions: substrate (1 mmol), acetonitrile (5 mL), VC-3 (20 mg), H₂O₂ (6 mmol), 36 watt domestic bulb, 70 $^{\rm o}$ C. b Isolated yield.

0.5

92

noting that properties of substituent groups have an important effect on the formation of desired products. An electron withdrawing group either on the aromatic ring or on the exocyclic double bond will inhibit the oxidation of substrate and

cause low yield of products (entries 9, 10). Besides of these, the conjugation of the aromatic ring with the exocyclic double bond is beneficial to the catalytic system (entry 12). Little product is obtained when substrate is not conjugated (entry 11).

4. Conclusion

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In conclusion, we have prepared $V_2O_5/g-C_3N_4$ composites through a mild method of wet impregnation and calcination, using ammonium metavanadate and melamine as precursors.

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The structure and composition of the as-prepared composites were characterized by various techniques. Among those prepared samples, the VC-3 catalyst was found to show optimal efficiency and give 98.7% conversion of styrene with 88.4% selectivity for benzaldehyde under visible light irradiation for 1h, using H_2O_2 as oxidant. A plausible photocatalytic mechanism has been proposed based on the oxidation results. This noble metal free catalytic system could also selectively convert a wide scope of styrene derivatives to the corresponding aldehydes with high yield (up to 92%). And the substituent at *ortho*-position will hamper the oxidation, while electron-donating group and the conjugation of the aromatic ring with the exocyclic double bond are beneficial for this transformation.

Conflicts of interest

There are no conflicts to declare.

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