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Metal-Free Allylic Oxidation with Molecular Oxygen Catalyzed by g-C_3N_4 and *N*-Hydroxyphthalimide

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Abstract Polymeric graphitic carbon nitride (g-C_3N_4) is a layered graphite-like nitrogen-rich material, bearing the potential ability to reductively adsorb molecular oxygen for catalytic allylic oxidation. Furthermore, *N*-hydroxyphthalimide (NHPI) has been recognized as an efficient catalyst for aerobic oxidation of various organic compounds under mild conditions in the presence of various co-catalysts. We present here a promising strategy for employing such nitride-rich g-C_3N_4 combined with NHPI to form an all-organic metal-free composite and have examined its activity for allylic oxidation with molecular oxygen as the primary terminal oxidant. In the case of allylic oxidation α-isophorone catalyzed by g-C_3N_4/NHPI gave priority to its corresponding carbonyl compound and epoxide. The effects of various reaction conditions on the catalytic reaction were optimized, affording 74.8 % conversion with 44.4 % selectivity of ketoisophorone at 130 °C in 5 h. Repeated runs demonstrated that the catalyst was stable for at least three cycles without noticeable loss of its catalytic activity.

Keywords Allylic oxidation · g-C_3N_4 · *N*-Hydroxyphthalimide · Molecular oxygen

1 Introduction

Selective allylic oxidation has been studied comprehensively over the past decade, for its extensive application in organic synthesis and industrial chemistry [1, 2]. Of the variety oxidants employed so far, the noteworthy examples include metal salts (SeO_2 [3], CrO_3 [4]), tert-butyl hydroperoxide (TBHP) [5], hydrogen peroxide (H_2O_2) [6] and molecular oxygen (O_2) [7, 8]. Among these oxidants, although metal salts could obtain ideal conversion and selectivity, they bore certain defects such as environmental hazards, high expense and waste of metal resources. TBHP and H_2O_2 are obviously more environmentally benign than metal salts, however, for safety, there is a need to remove the excess oxidants, except that, TBHP is so expensive for large-scale industrial application. Molecular oxygen is cheap, forms water as the only by-product and obtains maximum atom efficiency [9], O_2 is more ideal oxidant for both economical and environmental benefits. However, molecular oxygen is a relatively unreactive oxidation toward the strong bonds of C–H for its triplet ground state structure [10]. Heretofore, many catalysts which can efficiently catalyze allylic oxidation with molecular oxygen have been reported, such as heteropoly acid [11], phthalocyanine [12], Schiff-base transition metals (Mn, Cu, Co, Ni) [13–15]. Even so, rigorous solvent (DMSO) [11] and combination with metal ions made them unacceptable for the sustainability of the process. Bearing in mind these concepts, efficient metal-free catalyst, which can active molecular oxygen, is indispensable from the eco-friendly point of view.

In our preceding papers, the organic catalyst, *N*-hydroxyphthalimide (NHPI) has been recognized as a remarkable catalyst for aerobic oxidation of various organic substrates via hydrogen abstraction by intermediate phthalimide-*N*-oxyl (PINO) radical [16]. Although the generation of the PINO radicals through the precursors NHPI can be achieved efficiently by using transition metal salts [10, 16, 17] as the mediators, the catalytic system is detrimental to environment. Green chemistry teaches us

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that there is an urgent need for eco-friendly methods to carry out organic reactions. Then creating a system based on NHPI and a recoverable co-catalyst is one feasible access to obviate this disadvantage. Currently, a nitrogen-rich graphitic carbon nitride (g-C_3N_4) [18, 19], a solid-state semiconductor, has attracted much attention. This material resembles the polymeric melamine and is regarded as the most stable allotrope of covalent carbon nitride solids at ambient conditions, owing to the fact that it is formed by the *sp*^{2} hybridization of carbon and nitrogen generating the heptazine heterocyclic ring (C_6N_7) unit, later that the rings are linked by edge N forming the $\prod$ conjugated graphitic layers [20]. Beyond that, g-C_3N_4 exhibits good stability, ease of reusability, electronic and catalytic properties [21], which make it promising applications as heterogeneous metal-free catalysts for selective alcohol oxidation [22], coupling of amines [23], selective oxidation of primary carbon hydrogen bonds [21], and hydrogen evolution by splitting water [24]. Very recently, Li and co-workers [25] have applied g-C_3N_4 assisted by *N*-hydroxy compounds in selective allylic oxidation with molecular oxygen under visible light irradiation. However, visible light spectrum (400–800 nm) only takes possession 46 % of the solar spectrum. In addition, common glass apparatus is of inhibition effect on the absorption of light, and the quartz glass instrument is demanded. Employing stainless steel autoclave as reaction vessel under heating alone is more convenient for industrial production. Inspired by these previous findings, we would like to build a catalytic system of combining g-C_3N_4 with NHPI as catalyst and molecular oxygen as the primary terminal oxidant in the allylic oxidation under heating alone within stainless steel autoclave, which is unprecedented and seems to be a intriguing method for converting hydrocarbons into their corresponding carbonyl compounds.

2 Experimental

2.1 Materials and Methods

All the chemicals were of analytical grade apart from industrial-grade α-isophorone. They were commercially purchased and used without further treatment. Infrared spectra were determined on a Nicolet NEXUS 670 FT-IR spectrophotometer using KBr discs in the 400–4,000 cm^{-1} region. Powder X-ray diffraction (XRD) patterns of the heterogeneous samples were measured with Rigaku D/Max III VC diffractometer with Cu KR radiation at 40 kV and 40 mA in the range of $2\theta = 2$–$9°$. The reaction products of oxidation were determined by AGILENT QP2010 GC/MS instrument and analyzed by GC-7890II gas chromatograph with a 50 m × 0.25 mm × 0.25 μm OV-1701 column.

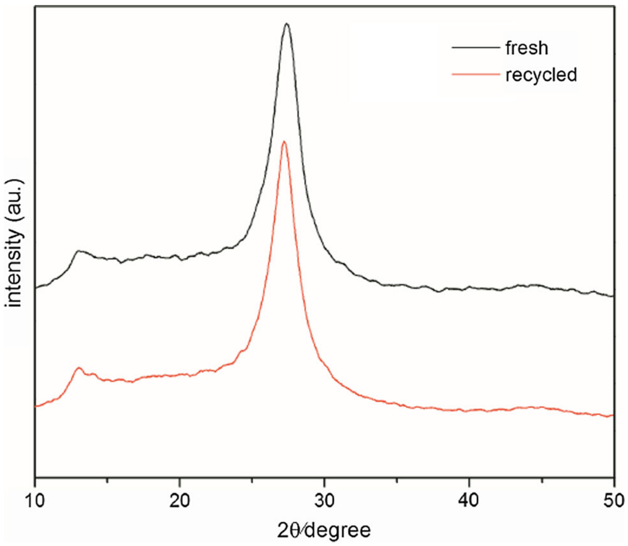


Fig. 1 XRD patterns of g-C_3N_4 materials

2.2 Preparation of Catalyst

The g-C_3N_4 was prepared by heating melamine directly according the previous reports [26, 27]. In a typical procedure, melamine was put into an alumina crucible with a cover, heated at a rate of 3 °C/min reaching temperature of 550 °C in a muffle furnace, treated at this temperature for further 4 h. When cooling to room temperature, grinding the pale yellow polymer obtained the g-C_3N_4 powder.

2.3 Oxidation Reaction

Reactions were carried out in a 100 mL stainless steel autoclave with a magnetic stirrer. α-Isophorone (α-IP, 10 mmol), solvent acetonitrile (10 mL) were placed in the vessel together with g-C_3N_4 (200 mg), NHPI (1 mmol, 10 mol%), and the reactor was sealed. Prior to heating to desired temperature (130 °C) under stirring, the atmosphere over the autoclave reactor was replaced three times with O_2 and pressurized with O_2 (1.2 MPa). When the reaction was finished, the autoclave reactor was cooled to the ambient temperature and slowly depressurized. The reaction mixture was analyzed by GC–MS and GC.

3 Results and Discussion

3.1 Characterization of g-C_3N_4

In Fig. 1, XRD patterns of the samples show the characteristic (002) interplanar stacking peak around 27.4°, corresponding to the interlayer distance of aromatic systems of d = 0.326 nm, suggesting the formation of well-built

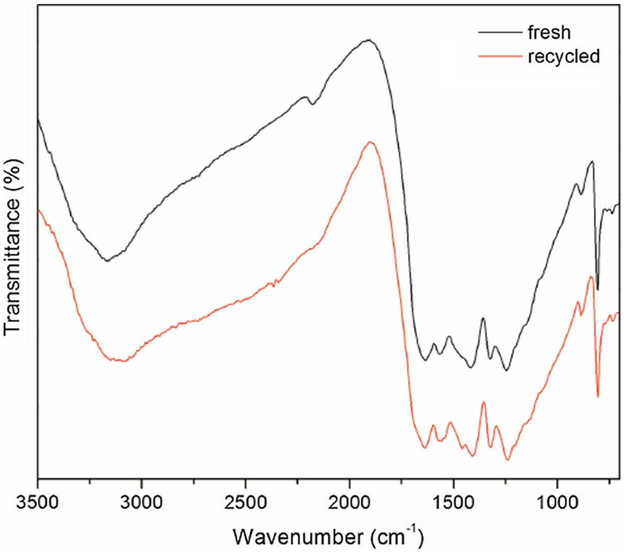


Fig. 2 The FT-IR spectra of fresh and used g-C_3N_4

g-C_3N_4 layer structure [28]. Another peak at 13.1° agrees with (100) interplanar of tri-triazine units, which is indexed as the 100 peak [29]. Anything else, no obvious difference can be detected between the recycled and fresh g-C_3N_4, which indicates that the g-C_3N_4 is of good stability.

The FT-IR spectra of fresh and recycled g-C_3N_4 are shown in Fig. 2. Several bands in the 1,200–1,600 cm^{-1} are ascribed to the stretching vibration of the heterocyclic aromatic ring units, while the sharp absorption peak at 800 cm^{-1} is considered as the characteristic breathing mode of the triazine cycle [30]. In addition, the broad absorption peak located at 3,000–3,300 cm^{-1} corresponding to the N–H components (uncondensed amino) and the O–H bands (the absorbed H_2O molecules) are observed [31]. Upon comparison, the fresh and recycled g-C_3N_4 bear similarity to each other, which correspond to the literature report.

Figure 3 depicts the scanning electron micrograph (SEM) images of fresh and recycled g-C_3N_4 and shows the typical stacked lamellar structure, and it has the basic characteristic of g-C_3N_4 of a graphite-like structure [30]. Beyond that, no obvious change of the catalyst g-C_3N_4 is viewed after the reaction.

3.2 Effect of Various Reaction Conditions on the Catalytic Reaction

3.2.1 Effect of Reaction Temperature and Time

The effects of reaction temperature and time on the oxidation were examined using 200 mg g-C_3N_4 and 5 mol% NHPI, and the results are shown in Table 1. As expected, the conversion of α-isophorone went up with the concomitant gradual increase of temperature and reached a maximum at 130 °C (entry 3) and then changed slightly even at higher temperature. However, no significant variation in the selectivity of ketoisophorone (KIP) was observed during the course of the reaction. This fact has mainly been caused by the following accounts: under low temperature, the energy was not sufficient for g-C_3N_4 to activate oxygen molecule, α-IP was hardly oxidized. As illustrated, with prolonging reaction time from 3 to 5 h, the conversion of α-IP increased from 33.9 to 60.7 % (entries 6 and 8). While as the reaction continued, the selectivity of KIP and α-IP conversion remained almost unchanged. Hence, 130 °C and 5 h should be the suitable reaction conditions.

3.2.2 Effect of Oxygen Pressure

It is interesting to note that the pressure of molecular oxygen has significant influence on the allylic oxidation of α-IP (Fig. 4). Below 1.2 MPa a positive impact of O_2 pressure on the reaction is observed clearly. The α-IP

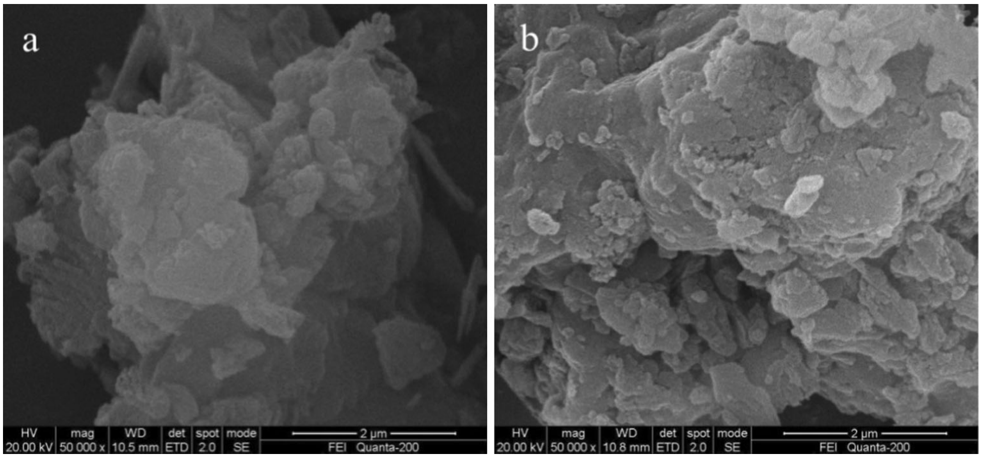


Fig. 3 SEM images of the samples. **a** fresh g-C_3N_4 and **b** used g-C_3N_4

Table 1 The effects of reaction temperature and time on α-IP oxidation

Entry	T (°C)	t/h	Conversion (%)	Selectivity (%)	
				KIP	OIP
1	110	5	35.1	47.7	15.4
2	120	5	49.1	34.9	18.9
3	130	5	60.7	42.4	21.7
4	140	5	57.6	39.9	20.7
5	150	5	56.0	34.4	21.7
6	130	3	33.9	42.6	27.8
7	130	4	46.3	43.6	24.2
8	130	5	60.7	42.4	21.7
9	130	6	56.8	46.2	22.5
10	130	7	55.1	43.5	22.9
11	130	8	52.0	42.1	24.6
12	130	9	50.8	44.2	25.7
13	130	10	54.0	41.9	26.3

Reaction conditions: 10 mmol α-IP, 200 mg g-C_3N_4 and 5 mol% NHPI, 10 mL CH_3CN, 1.2 MPa O_2. Analyzed by GC

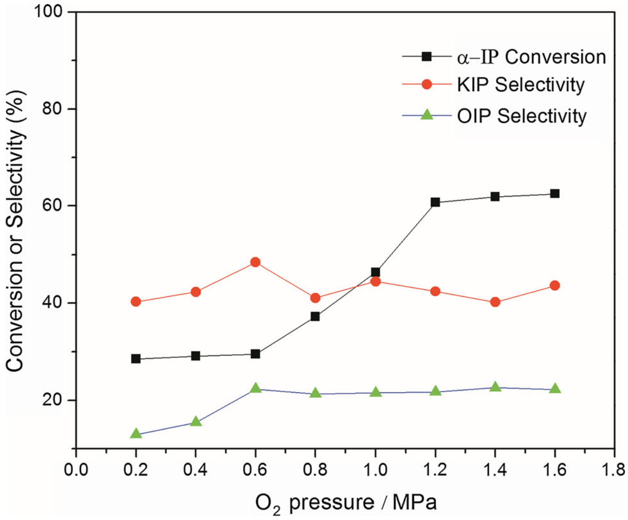


Fig. 4 The effect of O_2 pressure on α-IP oxidation

conversion improves from 29.5 to 60.7 % with increasing O_2 pressure from 0.6 to 1.2 MPa, and then changes very slightly after that. The selectivity of KIP has always been rather constant. It has been generally accepted that the dioxygen solubility in the liquid phase increases with the increase of dioxygen pressure. At a lower O_2 pressure, the O_2 concentration in solution is so low that insufficient O_2 could be activated by catalysts, which contributes to the lower conversion. When the oxygen solubility in the solution reaches saturation, excessive oxygen pressure has no much influence on the oxidation efficiency.

Table 2 The effects of g-C_3N_4 and NHPI amount on the α-IP oxidation

Entry	g-C_3N_4 (mg)	NHPI (mol%)	Conversion (%)	Selectivity (%)	
				KIP	OIP
1	100	5	53.7	37.6	18.4
2	200	5	60.7	42.4	21.7
3	300	5	65.1	34.3	14.1
4	400	5	52.8	31.8	20.1
5	200	0	8.7	24.4	26.5
6	0	5	23.5	41.9	7.0
7	200	2.5	24.6	39.7	24.1
8	200	7.5	66.9	42.9	19.6
9	200	10	74.8	44.4	12.0
10	200	1.25	67.1	43.8	14.0

Reaction conditions: 10 mmol α-IP, g-C_3N_4, NHPI, 10 mL CH_3CN, 1.2 MPa O_2, 130 °C, 5 h. Analyzed by GC

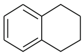
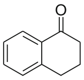
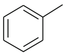
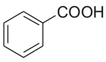
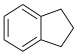
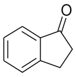
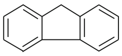
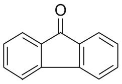
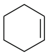
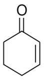
3.2.3 *Effect of Catalyst Amount*

From Table 2, it is observed that the conversion of α-IP improves with the increase of g-C_3N_4 amount until 300 mg (entries 1–3). After that, the conversion decreases slightly, due to the solution can't stir evenly. The selectivity decreases obviously (42.4 and 34.3 %, respectively) with increasing the amount of g-C_3N_4 from 200 to 300 mg. Taking both conversion and selectivity into consideration, 200 mg g-C_3N_4 is the suitable amount. Needless to say, it is difficult to promote this oxidation with g-C_3N_4 or NHPI alone (entries 5 and 6). To further make clear the effect of NHPI, different amount of NHPI was added into the reaction, the catalytic efficiency was achieved to the maximum using 10 mol% of NHPI with 74.8 % conversion of α-IP and 44.4 % KIP selectivity (entry 9). Even though more quantity of NHPI was added, the α-IP conversion and the KIP selectivity changed slightly (entry 10).

3.2.4 *Oxidation of Different Hydrocarbons Catalyzed by g-C_3N_4/NHPI*

To further probe the generality of this metal-free catalytic system, further researches were studied to oxidize various hydrocarbons by g-C_3N_4/NHPI with O_2 under heating alone (Table 3). Tetralin afforded a remarkably high conversion of 95.7 % towards the formation of tetralone with 60.1 % selectivity. In the case of oxidizing toluene, the benzoic acid was obtained as the main product giving 89.4 % conversion and 69.7 % selectivity (entry 2). Furthermore, the reaction system was found to be acceptable for oxidizing indane and fluorene to indanone and fluorenone affording the satisfactory selectivity of 72.2, 87.3 %

Table 3 Oxidation of various hydrocarbons by the g-C_3N_4/NHPI

Entry	Substrate	Product	Conv.(%)	Sel. (%)
1			95.7	60.1
2			89.4	69.7
3			54.3	72.2
4			66.4	87.3
5			64.9	82.1

Reaction conditions: substrates 10 mmol, g-C_3N_4 200 mg, NHPI 5 mol%, acetonitrile 10 mL, O_2 1.2 MPa, 130 °C, 5 h. Analyzed by GC

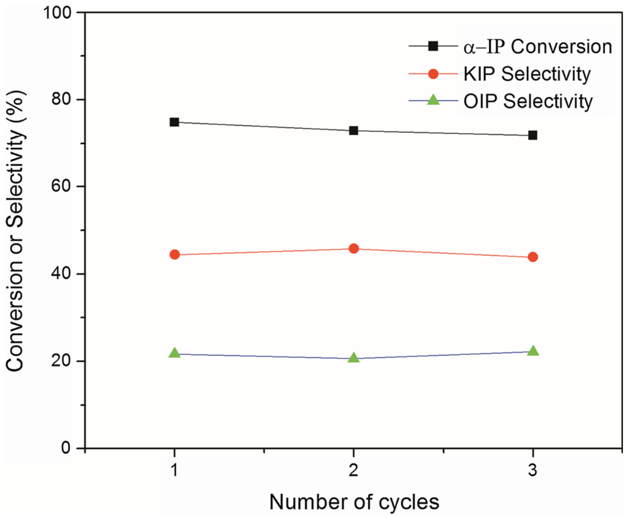


Fig. 5 Recycling study of the catalyst

and the conversion of 54.3, 66.4 %, respectively (entries 3 and 4). 64.9 % cyclohexene was also converted into corresponding 2-cyclohexene-1-one with 82.1 % selectivity (entry 5).

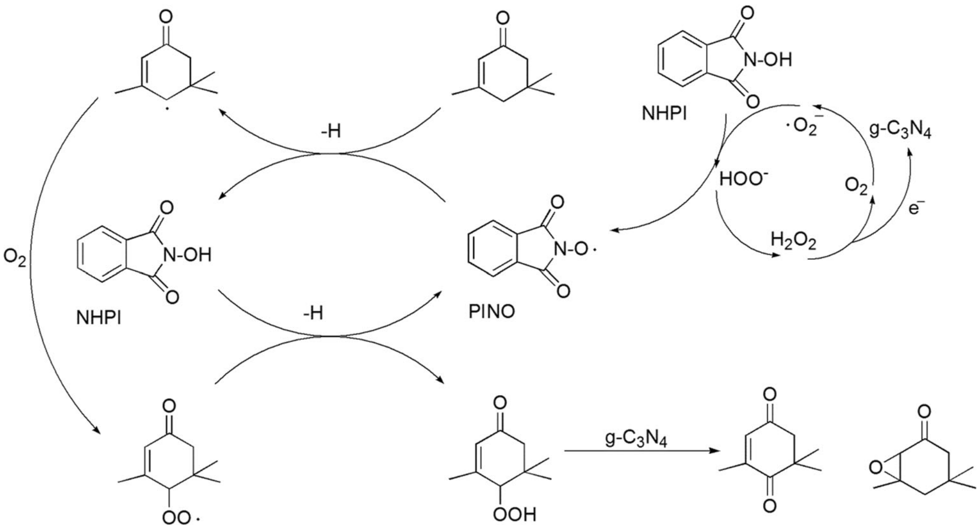
3.2.5 *Proposed Oxidation Mechanism*

Based on the results, a possible catalytic mechanism of g-C_3N_4/NHPI in the allylic oxidation of α-isophorone is proposed and is given in Scheme 1. The electrons in g-C_3N_4 can be activated and transmit from valence band to conduction band under heating [32, 33]. The superoxide radical anion (O_2^{-}) formed by molecular oxygen absorbing the excited electrons from the conduction band of the g-C_3N_4 [22], captures a hydrogen from NHPI generating PINO. At the same time, the O_2^{-} forms HOO^{-} which can oxidize another NHPI to PINO. Then, PINO abstracts a hydrogen atom from α-IP forming α-IP radical, while PINO itself converted into NHPI again [34]. Synchronously, the newly formed α-IP radical is trapped by O_2 producing peroxy radical, which finally results in oxygenated products.

3.2.6 *Reused of g-C_3N_4*

After the first oxidation reaction, the g-C_3N_4 can be easily recovered simply by washing with 0.2 M NaOH [22] and then dried in a vacuum oven at 65 °C overnight. Then, the obtained g-C_3N_4 was used directly in subsequent reaction cycles and no obvious loss of its catalytic activity and selectivity were observed, as shown in Fig. 5, giving 74.8, 72.9, 71.8 % conversion for the first, second, third runs,

Scheme 1 The proposed mechanism for the oxidation reaction



respectively. That means the g-C_3N_4 was stable in the catalytic reaction media.

4 Conclusion

In summary, the fangled metal-free, heterogeneous catalysis protocol consisting of g-C_3N_4 combined with NHPI was applied to catalyze allylic oxidation of α-isophorone into ketoisophorone using molecular oxygen as the primary terminal oxidant. 74.8 % conversion of α-IP and 44.4 % selectivity of KIP were obtained under optimized reaction conditions (10 mmol α-IP, 200 mg g-C_3N_4, 10 mol% NHPI, 1.2 MPa O_2, 130 °C, 5 h). This catalytic process could eliminate the employment of any metal derivative, g-C_3N_4 was found to be stable and reusable. The clean and one pot reaction process described here provided a potential way to oxidize various compounds possessing these analogous structures.

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