DOI: 10.1002/adsc.201100175

Visible-Light-Induced Metal-Free Allylic Oxidation Utilizing a Coupled Photocatalytic System of g-C_3N_4 and *N*-Hydroxy Compounds

Pengfei Zhang,[a] Yong Wang,[a,b] Jia Yao,[a] Congmin Wang,[a] Chao Yan,[a]
Markus Antonietti,[b] and Haoran Li[a,]*

[a] Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China
Fax: (+86)-571-8795-1895; phone: (+86)-571-8795-2424; e-mail: lihr@zju.edu.cn
[b] Department of Colloid Chemistry, Max-Planck Institute of Colloids and Interfaces, Research Campus Golm, 14424 Potsdam, Germany
Fax: (+49)-331-567-9502

Received: March 11, 2011; Revised: March 28, 2011; Published online: May 23, 2011

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201100175.

Abstract: Graphitic carbon nitride (g-C_3N_4) and *N*-hydroxy compounds can function as a non-metal photocatalytic system to activate O_2 for the selective allylic oxidation under mild conditions, avoiding the employment of any metal derivative or organic oxidizing agents. Interestingly, the novel photocatalytic system affords a remarkably high selectivity towards the formation of aldehydes, especially in the oxidation of toluene. By combining the unique nature of g-C_3N_4 (surface basicity, semiconductor features, high stability) and the remarkable catalytic oxidation reactivity of nitroxyl radicals, this photocatalytic system opens up a mild and efficent access for C–H bond activation.

Keywords: carbon nitride; C–H activation; *N*-hydroxyphthalimide; metal-free oxidation; NHPI; photooxidation

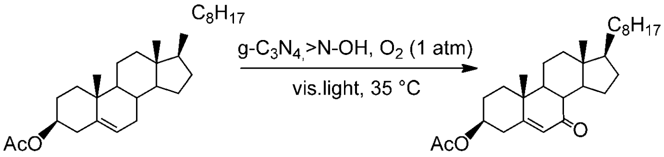
Selective allylic oxidation with molecular oxygen as the terminal oxidant is a primary and essential tool for organic synthesis and industrial chemistry, as it is believed that introduction of oxygen atoms into C–H bonds through aerobic oxidation is the cheapest way to synthesize more complex molecules from natural petroleum.[1] However, due to the triplet ground state structure, oxygen is a relatively unreactive molecule under mild conditions, especially towards strong C–H bonds. Traditional allylic oxidation is usually accompanied by the use of transition metal-containing catalysts under relatively harsh conditions (high temperature and high pressure), and it also suffers from limited conversion and selectivity.[2] From the standpoint of green and sustainable chemistry, metal-containing catalysts with high toxicity and expense should be avoided.

Metal-free catalysts have been becoming increasingly attractive in recent years, and considerable effort has been made to examine the effect of metal-free catalytic systems on the aerobic oxidation.[3] Recently, carbon nitrides have attracted considerable attention partly because of their potential applications in sustainable chemistry as metal-free heterogeneous catalysts.[4] For example, a recent break-through was achieved with the use of these materials as photocatalysts for the oxidation of alcohols and amines by O_2 under visible light irradiation.[5] These metal-free oxidation processes are good for the proof of principle, the activity of bare carbon nitride was, however, generally very low which makes the practical application difficult. Some modifications of carbon nitride were found to show improved activities in the oxidation reactions.[6] However, it is still difficult to drive the oxidation of sp^3 C–H bonds (for example: toluene and cyclohexane) with carbon nitrides and O_2.

In the past decade, some *N*-hydroxy compounds, acting as a new kind of organocatalyst, such as 1-hydroxybenzotriazole (HBT), *N*-hydroxysuccinimide (NHSI), and *N*-hydroxyphthalimide (NHPI), have attracted interest in a broader way.[7] For example, *N*-hydroxy compounds (>N-OH) can act as a hydrogen donor and be oxidized to the *N*-oxyl radical (>N-O$^•$), which is a neat and selective oxidant for the transformation of hydrocarbons, like alkanes and alkylaromatics. However, co-catalysts (particularly metal salts) are necessary for the *N*-hydroxy compound (>N-OH) to generate the *N*-oxyl radical (>N-O$^•$).[7g,8]

Can carbon nitrides bridge the gap between visible light energy and *N*-hydroxy compound (>N-OH) irradiation? Based on the previous reports, graphitic carbon nitride (g-C_3N_4) can activate O_2 to $O_2^{\bullet-}$ under the illumination of visible light.[5,9] This suggested to us that if $O_2^{\bullet-}$ can abstract a hydrogen from >N-OH, the formed >N-O$^\bullet$ radical could smoothly activate the C–H bond. To test this interesting hypothesis, a combination of g-C_3N_4 and HBT was used for the selective allylic oxidation of cholesteryl acetate (CA) to 7-ketocholesteryl acetate (7-KOCA), which is a key step in the synthesis of vitamin D_3 (Table 1).[10]

Table 1. The results of the oxidation of cholesteryl acetate with g-C_3N_4 and *N*-hydroxy compounds.[a]



Entry	Catalyst	*hv*	Conv. [%]	Sel. [%]
1	g-C_3N_4 (100 mg)/HBT (1 mmol)	+	23	61
2	g-C_3N_4 (100 mg)	+	<1	–
3	HBT (1 mmol)	+	<1	–
4	g-C_3N_4 (100 mg)/NHSI (1 mmol)	+	19	96
5	g-C_3N_4 (100 mg)/NHPI (1 mmol)	+	48	>99
6	NHSI (1 mmol)	+	<1	–
7	NHPI (1 mmol)	+	3	67
8	g-C_3N_4 (100 mg)/DMG (1 mmol)	+	<1	–
9	g-C_3N_4 (100 mg)/NHPI (1 mmol)	–	4	73
10[b]	g-C_3N_4 (100 mg)/NHPI (1 mmol)	–	44	>99
11[c]	g-C_3N_4 (100 mg)/NHPI (1 mmol)	–	38	62
12	g-C_3N_4 (50 mg)/NHPI (1 mmol)	+	22	>99
13	g-C_3N_4 (100 mg)/NHPI (0.5 mmol)	+	9	>99
14[d]	BPO/NHPI (1 mmol)	–	20	54
15[e]	AQ/NHPI (1 mmol)	–	<1	–
16[f]	Co(acac)$_2$/NHPI (1 mmol)	–	45	78

[a] *Reaction conditions:* cholesteryl acetate (10 mmol), acetone solvent (80 mL), O_2 1 atm, 35 °C, 8 h, under visible light irradiation.

[b] The reaction was carried out with visible light irradiation for 2 h and then in the dark for 6 h.

[c] g-C_3N_4 was separated out after the reaction had been carried out for 2 h.

[d] BPO: benzoyl peroxide, 0.05 mmol.

[e] AQ: anthraquinone, 0.1 mmol.

[f] Co(acac)$_2$: cobalt(II) acetylacetonate, 0.05 mmol.

To our delight, when the g-C_3N_4/HBT system was employed as catalyst under visible light, 23% of CA was transformed to 7-KOCA with 61% selectivity (entry 1, Table 1), while g-C_3N_4 or HBT alone was not efficient for the transformation of CA (entries 2 and 3, Table 1). These results illustrated that g-C_3N_4 and HBT were coupled as a catalytic system for the oxygenation of CA, as expected.

When NHSI was used in place of HBT, a relatively good selectivity (96%) was obtained with similar conversion (19%) (Entry 4, Table 1). Encouraged by those results, the combination of g-C_3N_4 and NHPI was examined, in which a good result (48% conversion and >99% selectivity) was obtained (entry 5, Table 1). This result is consistent with previous observations that NHSI is less reactive than NHPI in the oxidation of fluorene.[7f] Needless to say, it was difficult to promote this oxidation with NHSI or NHPI alone (entries 6 and 7, Table 1). The simple and cheap *N*-hydroxy compound, dimethylglyoxime (DMG) in combination with NHPI, showed no photocatalytic activity in the transformation of CA (entry 8, Table 1).

The H-abstraction reaction from R–H by the >N-O$^\bullet$ radical is an important step in the oxidation of hydrocarbons catalyzed by *N*-hydroxy compounds. The bond dissociation energy (BDE) of the >NO–H bond is closely related to H-abstraction process by the >N-O$^\bullet$ radical.[11] In the oxidation of CA, HBT exhibited a lower reactivity than NHPI, which can be rationalized on the basis of the lower energy of the >NO–H bond of HBT, if compared with the corresponding >NO–H bond energy of NHPI (85 *vs.* 88 kcal mol^{-1}, respectively).[7b] These results provide an argument that the lower BDE of the >NO–H bond is, the easier is the corresponding >N-O$^\bullet$ radical formed with H-abstraction by $O_2^{\bullet-}$. However, the easily formed >N-O$^\bullet$ radical shows weak or even no ability for abstracting hydrogen from hydrocarbons[7f,g]. Since the g-C_3N_4/NHPI system presented excellent catalytic activity in oxygenationof CA, this system was selected for further studies.

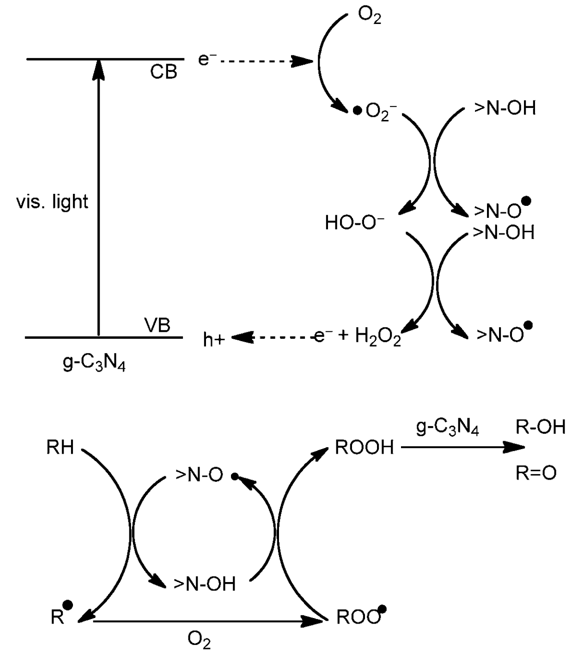
To clarify the role of g-C_3N_4 and *N*-hydroxy compounds, detailed investigations have been carried out on the oxidation of CA. When the process was carried out in the dark, only 4% conversion of CA was observed under the same system (entry 9, Table 1). It was surprising that almost the same resulting (44% conversion and >99% selectivity) was obtained when the oxidation was performed under visible light irradiation for 2 h and then in the dark (entry 10, Table 1). This result suggested that g-C_3N_4 may act as initiator for the generation of phthalimide *N*-oxyl radical (PINO) to some extent. To further make clear the role of g-C_3N_4, we separated g-C_3N_4 out by filtration after the oxidation had been carried out under visible light irradiation for 2 h and a slightly lower conversion 38% with 62% selectivity was achieved

(Entry 11, Table 1). The lost selectivity of about 38% is believed to be due to 7-hydroperoxide-cholesteryl acetate, which was observed as the only side product in this oxidation. It is evident that g-C_3N_4 demonstrates some Lewis base character which can promote the decomposition of 7-hydroperoxide-cholesteryl acetate.[12] When amount of NHPI or g-C_3N_4 was halved under these conditions, lower conversions (22%, 9%) were achieved, while keeping the selectivity at >99% (entries 12 and 13, Table 1). Early research indicated that NHPI can efficiently oxidize substrates with molecular oxygen upon adding a small amount of co-catalysts. Compared with these catalytic systems, g-C_3N_4/NHPI system exhibits an excellent catalytic effect and especially a high selectivity for ketones (entries 14–16, Table 1).

A plausible reaction pathway for the allylic oxidation by g-C_3N_4/>N-OH under visible light irradiation is illustrated in Scheme 1. The visible-light-induced catalytic cycle is assumed to involve two coupling steps of electron transfer: (i) O_2 captures the light-excited electron from the conduction band (CB) of g-C_3N_4 to generate superoxide radical anion ($O_2^{\bullet-}$); (ii) after abstracting a hydrogen from >N-OH, $O_2^{\bullet-}$ is reduced to HOO^-. Then HOO^- can react with the positive hole (h+) by injecting a electron into the valence band (VB) of g-C_3N_4, at the same time oxidizing another >N-OH to >N-O$^\bullet$. The nitroxyl radicals, notably phthalimide *N*-oxyl (PINO) follow a free radical route, initiating by abstracting a hydrogen atom from RH. Under an O_2 atmosphere the newly formed R$^\bullet$ is rapidly trapped by O_2 to give a ROO$^\bullet$ radical, which subsequently abstracts a hydrogen atom from >N-OH to form >N-O$^\bullet$. Finally, g-C_3N_4 catalyzes the decomposition of intermediate ROOH to the oxygenated products.

The superoxide radical anion ($O_2^{\bullet-}$) formed by the reduction of O_2 (by the excited electrons from the conduction band of the g-C_3N_4) was confirmed by electron spin resonance (ESR) and the DMPO (5,5-dimethyl-1-pyrroline *N*-oxide) spin trap technique in methanol (Figure 1).[13] When NHPI was added to this system, the ESR signals for DMPO-$O_2^{\bullet-}$ adducts decreased under the same conditions. The change in the ESR signal corresponds to the oxidation of NHPI to PINO by $O_2^{\bullet-}$. On the basis of that result, we believe that some *N*-hydroxy compounds with suitable BDE values all can be oxidized to their corresponding nitroxyl radicals by $O_2^{\bullet-}$ and then catalyze a wide variety of free radical oxidations.

To further probe the potential of this metal-free photocatalytic system, various substrates were oxygenated by g-C_3N_4/NHPI system with O_2 under visible light (Table 2). Cyclohexene was oxygenated smoothly to afford 2-cyclohexen-1-one as the main product (entry 1, Table 2). To test the reusability of g-C_3N_4 which can be easily recovered by simple filtration and washing with 0.2 M NaOH, three recycling runs were carried out on the oxidation of cyclohexene. g-C_3N_4 can be reused at least three times without losing activity (entries 2–4, Table 2). Phenylethylene, α-isophorone, α-pinene, and ethylbenzene were oxidized with a good selectivity (66–84%) for ketones, although the conversion (26–71%) was only moderate (entries 5–8, Table 2). The oxidation of β-isophorone was quick,



Scheme 1. Proposed potential oxidation mechanism for the g-C_3N_4/>N-OH system.

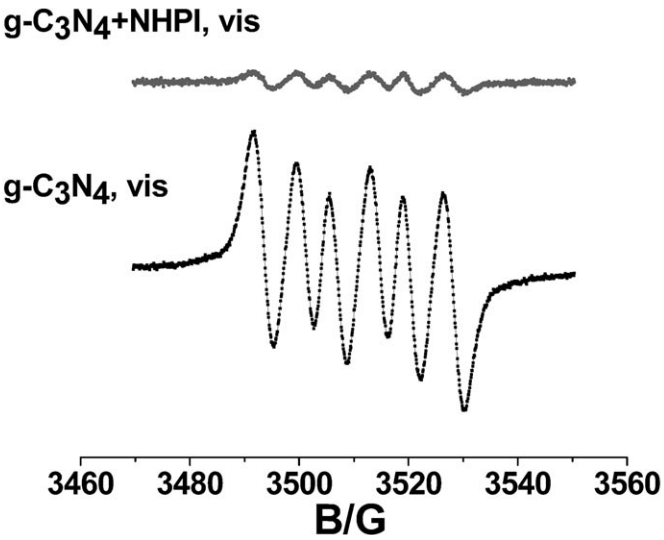
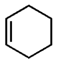
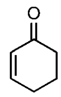
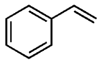
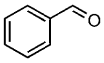
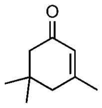
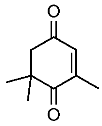
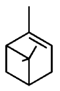
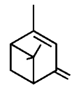
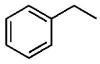
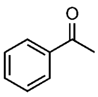
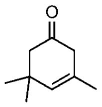
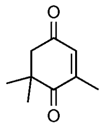
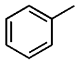
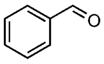
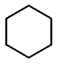
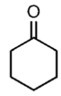


Figure 1. Changes in the DMPO spin-trapping ESR spectra for g-C_3N_4 (10 mg) and g-C_3N_4 (10 mg)/NHPI (50 mg) for superoxide radical ($O_2^{\bullet-}$) in methanol (1 mL). The mixture was stirred with bubbling O_2 and visible light irradiation for 10 min and then put into a quartz tube.

Table 2. The results of the oxidation of various substrates with g-C_3N_4 and NHPI.[a]

Entry	Substrate	Product	Time [h]	Conv. [%]	Sel. [%]
1			8	93	77
2[b]			8	92	71
3[c]			8	90	66
4[d]			8	95	67
5			24	33	70
6			20	26	79
7[e]			18	71	66
8			23	27	84
9[f]			4.5	100	> 99
10			20	9	> 99
11[g]			24	6	> 99

[a] *Reaction conditions: substrates* (10 mmol), g-C_3N_4 (100 mg), NHPI (1 mmol), acetonitrile (20 mL), O_2 1 atm, 60 °C, under visible light irradiation.

[b] Second run to test the reusability of catalyst.

[c] Third run to test the reusability of the catalyst.

[d] Fourth run to test the reusability of the catalyst.

[e] Benzonitrile (20 mL) as solvent.

[f] g-C_3N_4 (50 mg) and NHPI (0.5 mmol) were used.

[g] g-C_3N_4 (50 mg) and NHPI (0.1 mmol) were used.

giving 100% conversion and remarkably high selectivity (> 99%) towards the formation of keto-isophorone in 4.5 h (entry 9, Table 2). The oxidation of toluene gave benzaldehyde as the only product (> 99% selectivity) (entry 10, Table 2). Catalyzed by 50 mg of g-C_3N_4 with 0.1 mmol of NHPI, a 6% conversion of cyclohexane with cyclohexanone as the sole product (>99% selectivity) was obtained (entry 11, Table 2). As far as we know, in previous reports, no matter what co-catalyst was coupled, NHPI-catalyzed oxidations of toluene and cyclohexane all gave alcohols or acids as part of the product palette.[1a] It should be noted that when catalyzed by g-C_3N_4/NHPI (entries 10 and 11, Table 2), the oxidation products of toluene and cyclohexane were free of alcohols and acids, only benzaldehyde and cyclohexanone were detected. The g-C_3N_4/NHPI system is therefore rather selective, with respect to the aldehyde and ketone product it creates.

In summary, g-C_3N_4 asisted by *N*-hydroxy compounds has been successfully applied for selective allylic oxidations with molecular oxygen under mild conditions. Four *N*-hydroxy compounds have been tested in combination with g-C_3N_4, and the g-C_3N_4/NHPI system exhibits the best catalytic performance, affording high selectivities towards the formation of aldehydes and ketones, especially in the oxidation of toluene and cyclohexane. This visible-light-induced metal-free catalyst system opens up an efficient and mild access for selective oxidations with molecular oxygen. Moreover, we believe that various visible light-responsive materials can couple with *N*-hydroxy compounds, especially NHPI, and provide more metal-free catalyst systems for the oxidation of allylic C–H bonds.

Experimental Section

All the chemicals were of AR grade. They were commercially purchased and used without further treatment. A w-filament bulb (250 W) together with a 420 nm cut-off filter was used as a visible light source for the irradiation of the reaction system. The NMR spectra were recorded by Bruker ARX 500 NMR spectrometer, and TMS as the internal standard. Electron spin resonance (ESR) signals were recorded at room temperature (298 K) with a Bruker ESR A300 spectrometer. All GC experiments were carried out and recorded using a Shimadzu GC-2010. The structure of products and by-products was identified using an HP6890 GC/MS spectrometer by comparing retention times and fragmentation patterns with those of authentic samples.

General Procedure for the Oxidation of Cholesteryl Acetate

The oxidation of cholesteryl acetate (CA) was carried out in a three-necked glass-reactor (100 mL), which was fitted with an O_2 inlet tube and a reflux condenser. Cholesteryl acetate (10 mmol), catalysts as described in the Table and acetone (80 mL) were added to the reactor. A w-filament bulb (250 W) together with a 420 nm cut-off filter was placed at a distance of ~10 cm from the reactor as a visible light source for the irradiation of this reaction system. Then the reaction was performed at 35 °C in a water bath with O_2 flowing at a constant flow rate (20 mL min^{-1}) for 8 h. To carry out the reaction in the dark, the glass-reactor was covered with aluminium foil. Reactions were monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure at 50 °C. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/11) to afford 7-ketocholesteryl acetate (7-KOCA) as the desired product.

General Procedure for the Oxidation of the Substrates in Table 2

In a typical oxidation of the substrates in Table 2, 10 mmol of substrate, 100 mg of g-C_3N_4, 1 mmol of NHPI and of 20 mL acetonitrile were added into a 50-mL three-neck, round-bottom reactor, which was fitted with a magnetic stirrer and an O_2 inlet tube. The reaction was performed at 60 °C in a oil bath with fast stirring. The oxygen was flowing into the reactor at a constant flow rate (20 mL min^{-1}). After completion of the reaction, g-C_3N_4 was filtered and then the reaction mixture was injected into the GC for analysis with benzyl ethanoate as the internal standard. The products were confirmed by comparison with standard chemicals and GC-MS.

Reuse of g-C_3N_4

When the first oxidation had finished, after cooling down the reaction mixture to room temperature, g-C_3N_4 was separated by filtration. The yellow solid was washed with 0.2 M NaOH and then dried in a vacuum oven at 100 °C for 12 h. Finally, the recovered g-C_3N_4 was used in a subsequent reaction.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 20990221, 20803062 and J0830413). The authors are grateful to Zhejiang NHU Company Ltd, China, for financial support.

References

[1] a) F. Recupero, C. Punta, *Chem. Rev.* **2007**, *107*, 3800; b) T. Punniyamurthy, S. Velusamy, J. Iqbal, *Chem. Rev.* **2005**, *105*, 2330; c) J. Y. Mao, N. Li, H. R. Li, X. B. Hu, *J. Mol. Catal. A: Chem.* **2006**, 258; d) C. M. Wang, W. H. Guan, P. H. Xie, X. Yun, H. R. Li, X. B. Hu, Y. Wang, *Catal. Commun.* **2009**, *10*, 725.

[2] a) K. Weissermel, H. J. Arpe, *Industrial Organic Chemistry*, 3rd Completely Revised Edition, VCH, Weinheim, **1997**; G. W. Parshall, S. D. Ittel, *Homogeneous Catalysis*, 2nd edn., John Wiley and Sons, New York, **1992**, p 246.

[3] a) R. H. Fan, D. M. Pu, F. Q. Wen, J. Wu, *J. Org. Chem.* **2007**, *72*, 8994; b) X. L. Tong, J. Xu, H. Miao, *Adv. Synth. Catal.* **2005**, *347*, 1953; c) J. Zhang, Z. Wang, Y. Wang, C. Wan, X. Zheng, Z. Wang, *Green Chem.* **2009**, *11*, 1973; d) C. M. Wang, G. L. Wang, J. Y. Mao, Z. Yao, H. R. Li, *Catal. Commun.* **2010**, *11*, 758; e) G. Y. Yang, Y. F. Ma, J. Xu, *J. Am. Chem. Soc.* **2004**, *126*, 10542; f) G. Zheng, C. Liu, Q. Wang, M. Wang, G. Yang, *Adv. Synth. Catal.* **2009**, *351*, 2638; g) K. Matsunaka, T. Iwahama, S. Sakaguchi, Y. Ishii, *Tetrahedron. Lett.* **1999**, *40*, 2165; h) C. Einhorn, J. Einhorn, C. Marcadal, J. Pierre, *Chem. Commun.* **1997**, 447; i) R. Nakamura, Y. Obora, Y. Ishii, *Chem. Commun.* **2008**, 3417.

[4] a) Y. Wang, J. Yao, H. R. Li, D. S. Su, M. Antonietti, *J. Am. Chem. Soc.* **2011**, *133*, 2362; b) F. Goettmann, A. Fischer, M. Antonietti, A. Thomas, *Angew. Chem.* **2006**, *118*, 4579; *Angew. Chem. Int. Ed.* **2006**, *45*, 4467; c) F. Goettmann, A. Fischer, M. Antonietti, A. Thomas, *New. J. Chem.* **2007**, *31*, 1455; d) F. Goettmann, A. Thomas, M. Antonietti, *Angew. Chem.* **2007**, *119*, 2773; *Angew. Chem. Int. Ed.* **2007**, *46*, 2717; e) X. Jin, V. Balasubramanian, S. Selvan, D. Sawant, M. Chari, G. Q. Lu, A. Vinu, *Angew. Chem.* **2009**, *121*, 8024; *Angew. Chem. Int. Ed.* **2009**, *48*, 7884.

[5] a) F. Z. Su, S. Mathew, G. lipner, X. Z. Fu, M. Antonietti, S. Blechert, X. C. Wang, *J. Am. Chem. Soc.* **2010**, *132*, 16299; b) F. Z. Su, S. Mathew, L. Möhlmann, M. Antonietti, X. C. Wang, S. Blechert, *Angew. Chem.* **2011**, *123*, 683; *Angew. Chem. Int. Ed.* **2011**, *50*, 657.

[6] a) Y. Wang, J. S. Zhang, X. C. Wang, M. Antonietti, H. R. Li, *Angew. Chem.* **2010**, *122*, 3428; *Angew. Chem. Int. Ed.* **2010**, *49*, 3356; b) Y. Wang, H. R. Li, J. Yao, X. C. Wang, M. Antonietti, *Chem. Sci.* **2011**, *2*, 446; c) Y. Wang, Y. Di, M. Antonietti, H. R. Li, X. F. Chen, X. C. Wang, *Chem. Mater.* **2010**, *22*, 5120.

[7] a) C. Galli, P. Gentili, O. Lanzalunga, M. Lucarini, G. F. Pedulli, *Chem. Commun.* **2004**, 2356; b) P. Brandi, C. Galli, P. Gentili, *J. Org. Chem.* **2005**, *70*, 9521; c) E. Baciocchi, M. Bietti, M. D. Fusco, O. Lanzalunga, D. Raponi, *J. Org. Chem.* **2009**, *74*, 5576; d) E. Baciocchi, M. Bietti, O. Lanzalunga, A. Lapi, D. Raponi, *J. Org. Chem.* **2010**, *75*, 1378; e) R. Sheldon, I. C. E. Arends, *Adv. Synth. Catal.* **2004**, *346*, 1051; f) Y. Ishii, K. Nakayama, M. Takeno, S. Sakaguchi, T. Iwahama, Y. Nishiyama, *J. Org. Chem.* **1995**, *60*, 3935; g) G. Cantarella, C. Galli, P. Gentili, *J. Mol. Catal. B: Enzym.* **2003**, *22*, 135.

[8] a) Y. Ishii, T. Iwahama, S. Sakaguchi, K. Nakayama, Y. Nishiyama, *J. Org. Chem.* **1996**, *61*, 4520; b) S. Coseri, *Catal. Rev.* **2009**, *51*, 218.

[9] a) S. C. Yan, Z. S. Li, Z. G. Zou, *Langmuir* **2009**, *25*, 10397; b) S. C. Yan, Z. S. Li, Z. G. Zou, *Langmuir* **2010**, *26*, 3897; c) S. C. Yan, S. B. Lv, Z. S. Li, Z. G. Zou, *Dalton Trans.* **2010**, *39*, 1488.

[10] a) E. C. McLaughlin, H. Choi, K. Wang, G. Chiou, M. P. Doyle, *J. Org. Chem.* **2009**, *74*, 730; b) J. A. R. Salvador, J. H. Clark, *Green Chem.* **2002**, *4*, 352; c) Z. Yao, X. B. Hu, J. Y. Mao, H. R. Li, *Green Chem.* **2009**, *11*, 2013; d) M. A. Fousteris, A. I. Koutsourea, S. S. Nikolaropoulos, A. Riahi, J. Muzart, *J. Mol. Catal. A: Chem.* **2006**, *250*, 70.

[11] a) N. Koshino, Y. Cai, J. H. Espenson, *J. Phys. Chem. A.* **2003**, *107*,4262; b) B. Saha, N. Koshino, J. H. Espenson, *J. Phys. Chem. A.* **2004**, *108*, 425; c) Y. Sun, W. Zhang, X. Hu, H. Li, *J. Phys. Chem. B.* **2010**, *114*, 4862.

[12] a) Stamicarbon, European Patent EP 0092867, **1983**; b) X. X. Song, Y. X. Li, W. Wu, S. B. Fu, P. Yang, *Huagong Jinzhan.* **2004**, *23*, 322.

[13] J. R. Harbour, M. L. Hair, *J. Phys. Chem.* **1978**, *82*, 1397.