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Solvent-Free and Metal-Free Oxidation of Toluene Using O_2 and g-C_3N_4 with Nanopores: Nanostructure Boosts the Catalytic Selectivity

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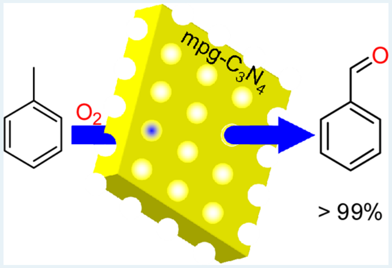
Supporting Information

ABSTRACT: Solvent-free oxidation of the primary C−H bonds in toluene to benzaldehyde has been achieved by using the metal-free catalyst g-C_3N_4 and O_2. It is the nanostructure of g-C_3N_4 that boosts the high selectivity by tuning the homogeneous oxidation to hetergeneous oxidation and capturing all free $\bullet O_2^-$ radicals to effectively suppress the overoxidation of aldehydes.



KEYWORDS: *heterogeneous catalysis, mesoporous materials, nanostructures, nitrides, selective oxidation*

Selective oxidation of primary carbon hydrogen bonds is of great importance in organic synthesis, and green, efficient, selective oxidation techniques are highly sought after in the chemical and pharmaceutical industry.[1−8] In view of a green catalytic oxidation process, molecular oxygen as the terminal oxidant, a recyclable and effective heterogeneous catalysts, and an inexpensive energy source are preferred.[1,3,8,9] When dioxygen is used in catalytic oxidations, the critical point is to promote selectivity of the catalyst to a single product among all the possible oxidation products at reasonable substrate conversion.[1,6,8,9] Toluene, as a typical alkyl aromatic molecule, can be oxidized to benzyl alcohol, benzaldehyde, benzoic acid, and benzyl benzoate, which are all commercially important intermediates in chemistry.[8] There have been many attempts to find a suitable catalystic system for toluene oxidation, but current catalysts have either offered low selectivity especially to benzyl alcohol and benzaldehyde with poor stability against overoxidation, or have required activated oxygen donors.[8] The use of supercritical CO_2 and ionic liquids as solvent has been investigated to promote the selectivity to benzaldehyde, but unfortunately resulted in very low conversions.[10,11] Commercial benzaldehyde is therefore mainly produced by the chlorination of toluene followed by saponification.[12] Recently, Hutchings and co-workers have shown that Au−Pd alloy nanoparticles are very effective for the selective oxidation of toluene with oxygen, giving high selectivity to benzyl benzoate under relatively mild solvent-free conditions. However, selective catalytic oxidation of primary carbon−hydrogen bonds in toluene to benzaldehyde in an oxygen-based system still remains a great challenge because of the overoxidation of the as-formed benzaldehyde with increased reactivity relative to toluene.[13−15]

The mildness and selectivity of enzymes greatly surpass those of conventional chemical catalysis presumably because of the geometric constraints that bring reacting species close together to accelerate their reaction and promote the selectivity of the unique product.[5,9,16−18] An important new area of organic chemistry is devoted to mimicking the enzymatic catalysis by organic scaffolds to get unprecedented powerful and selective catalysts.[5,9,16,17] Besides duplicating the structure and mimicking the active center of various enzymes, we and others reported the direct use of polymeric carbon nitride based materials in heterogeneous catalysis, indirectly following the intrinsic principles of enzyme catalysis.[18,19]

Polymeric carbon nitride can exist in several allotropes with diverse properties, but the graphitic phase (g-C_3N_4) is regarded as the most stable one under ambient conditions.[20] As a polymeric semiconductor, g-C_3N_4 exhibits high chemical stability, and high simplicity and versatility in engineering both the structure and composition and hence the catalytic, electronic and optical properties.[19−22] Recently, we have reported the catalytic or photocatalytic oxidation of amines, alcohols, and alkanes over g-C_3N_4 based catalysts, the activity and selectivity of which can be tuned by varying the doping atoms or nanofillers.[21−24] Toluene could also be oxidized over B-doped g-C_3N_4 by using H_2O_2 as the oxidant and acetonitrile as the solvent, whereby the selectivity to benzaldehyde was up to 99%.[22] However, this catalyst showed no activity in O_2-based catalytic oxidation of toluene.

Received: March 9, 2012
Revised: August 13, 2012
Published: August 31, 2012

Nanomaterials possess high surface areas and a high concentration of low-coordinated sites and surface vacancies, which are required for high catalytic performance.[25−39] Nanocatalysis as a potential bridge between homogeneous and heterogeneous catalysis could combine the advantages of both disciplines and offer unique activity with high selectivity in catalysis. However, current applications of nanocatalysts are mainly limited to the transition-metal-containing nanoparticles or carbon nanostructures.[25,34−39] Other metal-free materials, including carbon nitride and boron nitride, also promise great potentials as sustainable catalysts because of their good stability, inexhaustible resources, relatively low cost, rich surface functional groups, and ease of reusability.[21,27] In principle, fine engineering the microstructure of these metal-free materials into nanostructure could enrich surface functionalities and thus improve their electronic functions for enhancing catalytic activity. For example, generating nanoporous structures into the polymeric matrix of g-C_3N_4 has been proved to be able to enhance the efficiency of hydrogen production from the photochemical reduction of water by about 1 order of magnitude,[28] and offer novel activity in Friedel−Crafts reactions[29] and reductive fixation of CO_2.[30]

Herein, we report for the first time the selective oxidation of toluene and derivates to aldehydes over mesoporous g-C_3N_4 (mpg-C_3N_4) using O_2 under solvent-free conditions. The nanoporous structure of mpg-C_3N_4 based catalysts demonstrates morphology-dependent activity and selectivity in the oxidation of toluene, which is totally different to the activity of bulk g-C_3N_4.

The mpg-C_3N_4 materials used in this investigation were prepared by thermal condensation of cyanamide in the presence of a silica template, 12-nm SiO_2 nanoparticles. The detailed synthesis is described in the Supporting Information and Supporting Information, Table S1. For inorganic nanocatalysts, the size and crystal facets could significantly affect their catalytic performance. However, for carbon and carbon nitride based catalysts, surface area and structural defects usually dominate their property and also the catalytic activity. Simply by introducing different amounts of silica template according to modified synthetic methods previously described by our group, we could gradually tune the specific surface area of the sample from 8 m^2/g (g-C_3N_4) to 64 m^2/g (mpg60), 132 m^2/g (mpg130), and 301 m^2/g (mpg300). The specific surface area was demonstrated by the N_2 adsorption/desorption analysis (Figure 1a) and calculated by the Brunauer−Emmett−Teller (BET) model.

Unlike the more sheet-like structure of bulk g-C_3N_4 (Figure 2a), mpg130, as an example here, has non faceted pore walls around a pore system of spherical pores (Figure 2b and Supporting Information, Figure S1). The pore diameter is around 12−14 nm, which is consistent with the size of the silica template (12 nm). Both g-C_3N_4 and mpg-C_3N_4 samples have nearly the same the X-ray diffraction (XRD) patterns (Figure 1b) with only slight broadening of diffraction peaks in the nanoporous system, and also the same optical band gap can be estimated from the UV/vis spectrum (Figure 1c and Supporting Information, Table S1). These observations show that the silica nanoparticles just generate pores in the bulk material, but do not significantly disturb the local order of the polymer-like melon chains. The surface functionalities increase with the specific surface area because of surface termination. This can be proven by the infrared (FTIR) spectrum of the samples (Figure 1d). As compared with the FTIR spectra of g-C_3N_4, mpg-C_3N_4 exhibits gradually enhanced absorption peak around 3200 cm^{-1} that are indicative of secondary and primary amines; meanwhile the peaks of C−N heterocycle stretches of the extended network connection in the 1100−1600 cm^{-1} region are also very strong and sharp, again speaking for the well development of polymeric melon network in mpg-C_3N_4.[28,29]

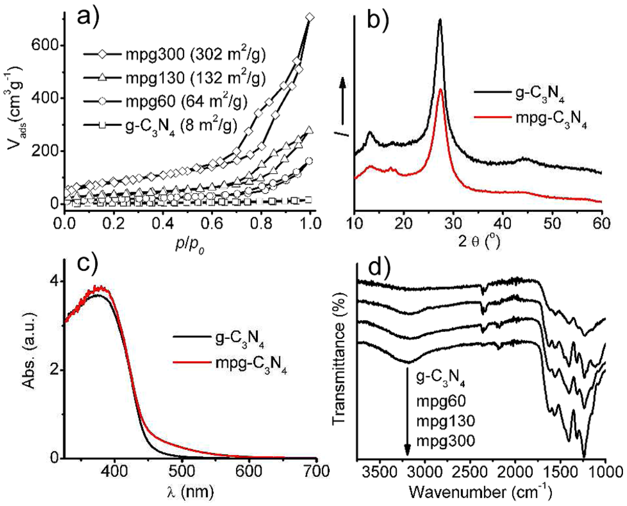


Figure 1. N_2 adsorption/desorption isotherms (a), XRD patterns (b), UV/vis spectra (c), and FTIR spectra (d) of g-C_3N_4 and mpg-C_3N_4 samples with different specific surface area. The mpg130 was taken as an example of mpg-C_3N_4 in panels b and c.

We then investigated mpg-C_3N_4 for the oxidation of toluene at 160 °C by using O_2 as the only oxidant in the absence of solvent. We run this reaction for security reasons in a "reactant-rich" mode, that is, the mixture is too rich in toluene to explode. By calculating the amount of toluene (94 mmol) and oxygen (44 mmol) in the reactor, it is clear that there is neither enough oxygen for the total conversion of the substrates nor to optimize the kinetics of the conversion. Thus, the final conversion numbers in this paper are limited by the insufficient amount of O_2 and only to be judged relative to each other. The main focus was to obtain high selectivity under those conditions, which then certainly can be transferred to a "real" conversion situation, involving a reactor with successive supply of high-press oxygen gas, which is however not within the research scope of current study.

Without any catalyst (Entry 1, Table 1), autoxidation of toluene into benzyl alcohol, benzaldehyde, benzoic acid, and benzyl benzoate can happen, whereby the selectivity to a distinct product is poor. When bulk g-C_3N_4 was used as the catalyst (Entry 2, Table 1), the conversion of toluene slightly decreased, while the selectivity of benzyl alcohol and benzaldehyde increased, but the control is still poor. This observation suggests that the involvement of g-C_3N_4, could partially moderate the homogeneous autoxidation of toluene into a heterogeneous oxidation at the surface of the material, but the surface functional groups are too limited to fully moderate the reaction.

Surprisingly, mpg130 could suppress the autoxidation of toluene completely and gave a very high selectivity (99%) to benzaldehyde (Entry 4, Table 1). When the O_2 gas was replaced by N_2 gas (Entry 5, Table 1), only trace amount of toluene were transferred to benzaldehyde with a selectivity of >99% presumably because of the absorbed O_2 on the surface of

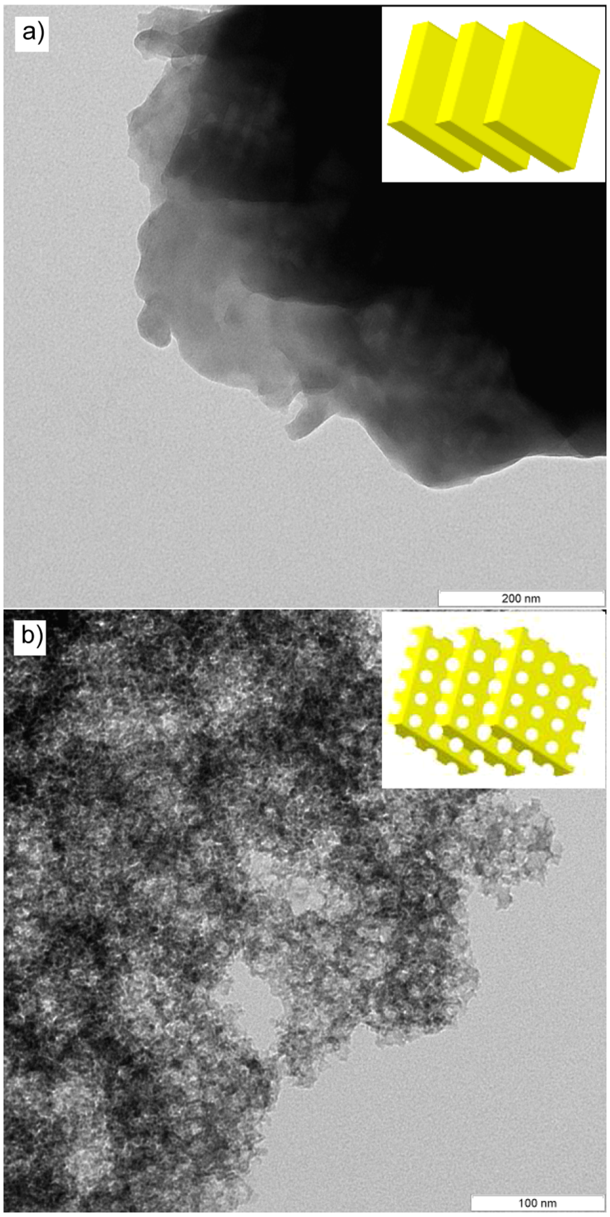
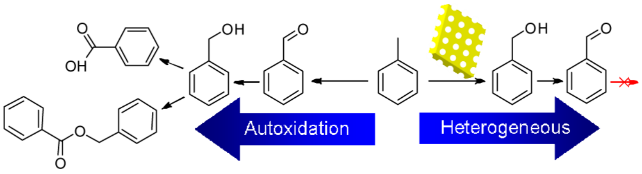


Figure 2. Typical transmission electron microscopy (TEM) images of g-C_3N_4 (a) and mpg130 (b). Insets: corresponding schematic structure.

Table 1. Reaction Conditions of Catalytic Oxidation of Toluene



				selectivity (%)[b]			
entry	catalyst	conditions[a]	con. (%)[b]	C=O	OH	acid	ester
1	No catalyst	160 °C, 16 h	33.7	22	30	40	8
2	g-C_3N_4 (100 mg)	160 °C, 16 h	24.4	24	29	34	3
3	mpg60 (100 mg)	160 °C, 16 h	23	35	29	35	1
4	mpg130 (100 mg)	160 °C, 16 h	2.6	>99			
5[c]	mpg130 (100 mg)	160 °C, 16 h	trace	>99			
6	mpg300 (100 mg)	160 °C, 16 h	3.1	>99			
7	mpg130 (100 mg)	160 °C, 4 h	1.9	>99			
8	mpg130 (100 mg)	160 °C, 48 h	2.7	>99			
9	mpg130 (50 mg)	160 °C, 16 h	8.5	66	8	26	
10	mpg130 (75 mg)	160 °C, 16 h	3.1	97	1	2	
11	mpg130 (1 g)	160 °C, 16 h	2.4	>99			
12	mpg130 (100 mg)	185 °C, 16 h	26	26	25	51	7
13	mpg130 (500 mg)	185 °C, 16 h	2.7	96	4		
14[d]	mpg130 (100 mg)	160 °C, 16 h	2.4	>99			
15[e]	mpg130 (100 mg)	160 °C, 16 h	2.6	>99			
16[f]	mpg130 (100 mg)	160 °C, 16 h	8.5	43	1	19	17
17[g]	mpg130 (100 mg)	160 °C, 16 h	trace	>99			
18	g-C_3N_4 (1.3 g)	160 °C, 16 h	9.6	50	9	40	1

[a] Typical conditions: 10 mL of toluene, catalyst, O_2 (10 bar), 160 °C, 16 h. [b] Conversions (%) and corresponding selectivities (%) to benzyl alcohol (OH), benzaldehyde (C=O), benzoic acid (acid), and benzyl benzoate (ester) were determined by GC-MS by using anisole as an external standard. [c] Reference experiments in the absence of O_2. [d] The catalyst was separated via centrifugation and washed with ethanol and 1 M NaOH solution for three times, and then reused in the third circle. [e] The catalyst was separated via centrifugation and washed with ethanol and 1 M NaOH solution for three times, and then reused in the fifth circle. [f] 20% (molar ratio of substrate) CH_3COOH was added. [g] 10% BHT was added

mpg-C_3N_4. We consider the heterogeneous oxidation of toluene to involve first an oxidation step of the semiconductor mpg-C_3N_4, leaving a surface-captured superoxide radical anion ($\bullet O_2^-$). The formation of superoxide radical anion, as previously observed in the oxidation of alcohol over mpg-C_3N_4,[33] can be further confirmed here by the addition of 10 mol % butylated hydroxytoluene (BHT) (Entry 17, Table 1), which is a terminating agent that can inhibit free radical chain process. This radical anion is bound as spin couple to the corresponding radical cation in the valence band of g-C_3N_4. This binding is presumably the source of selectivity, as free superoxide radicals give no selectivity to unique products and also favorably oxidized less-stable benzaldehyde to acid or ester as shown in Entry 1, Table 1. As expected, the intermittent conversion significantly fell to 2.6% because of the variation in oxidation mechanism from autoxidation to heterogeneous oxidation. This is why g-C_3N_4 is potentially better described as a moderator (rather than a catalyst), as acceleration of the reaction in fact does not take place. The turnover number (TON) of mpg-C_3N_4 (Supporting Information, Table S3) in current solvent-free reaction system is however much higher than that (TON: 0.16−0.33) of the boron-doped carbon nitride using H_2O_2 as the oxidant as described in our previous work.[22] Both the conversion and the selectivity (to benzaldehyde) of mpg-C_3N_4 catalyst are comparable or higher than supported Au or Pd nanoparticles under similar conditions calculated on the basis of the total mass of catalysts involved.[8]

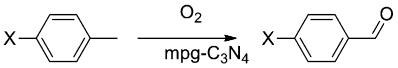
The effect of nanopores on suppressing the overoxidation of benzaldehyde and thus promoting its selectivity is better seen by testing carbon nitride based catalysts with varied pore volume. The less porous mpg60 is not effective enough to suppress the overoxidation of benzaldehyde (Entry 3, Table 1), while only the highly porous mpg130 and mpg300 (Entry 6, Table 1) could realize selectivities higher than 99% under the same conditions. When more bulk phase g-C_3N_4 (surface area: 10 m^2/g) was used as control sample, the final selectivity to benzaldehyde was improved but still poor (Entry 18, Table 1). These observations indicate that the enlarged surface area enhanced the selectivity by providing more active sites.

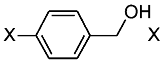
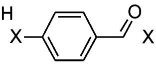
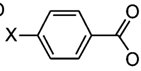
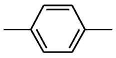
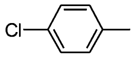
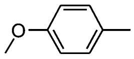
By varying the mass of catalyst (for example mpg130 here) used in the same reaction, we found that the minimum amount of catalyst for preserving high selectivity (Entry 9−10, Table 1) is around 75 mg at a reaction temperature of 160 °C. Raising the temperature from 160 to 185 °C increased the total conversion significantly, but the selectivity to benzaldehyde decreased to 26%. Adding more catalyst (500 mg of mpg130) could totally suppress the overoxidation of benzaldehyde (Entry 13, Table 1).

We can speculate that mpg-C_3N_4 could presumably bind both O_2 and toluene (via CT interactions) close together at the surface, while benzaldehyde is not strongly interacting and is released. This would be similar to the manner of enzyme catalysis. The surface-mediated character of the reaction was further confirmed via introducing additional CH_3COOH into the same catalytic system (Entry 16, Table 1), which can drive surfaced-tethered radicals, especially $\bullet O_2^-$, into the liquid phase and thus significantly decrease the catalytic selectivity (Supporting Information, Figure S2). The introduction of nanopores not only increased the surface area but also generated more active sites (uncondensed nitrogen functional groups). Thus, it is the number of active sites (Figure 1d) rather than the surface area that dominates the final catalytic performance of mpg-C_3N_4. However, there is no linear relation between the toluene conversion and the mass of catalyst. Adding too much catalyst (Entry 11, Table 1) or further extending the reaction time (Entry 7−8, Table 1) could not improve the final conversions of toluene. The very low conversions arise from, but are not limited to, the insufficient amount of O_2 in the reactor. On the other hand, there is also no linear relation between the toluene conversion and the pressure of O_2 gas (Supporting Information, Table S4). The detailed effects of the amount of catalysts, substrate molecules, and O_2 gas on the final catalytic activity are multivariate and complex. More studies are highly required in our future work to reveal the reaction mechanism and further optimize the catalytic performance of the mpg-C_3N_4 catalysts for real applications.

To test the general applicability of the mpg-C_3N_4 catalyst, we examined the efficacy of transformation of substituted toluenes to aldehydes under the same reaction conditions. Since mpg130 was found to be effective before, it was used in all further reactions. The mpg130 could moderate the oxidation of primary C−H bonds (Table 2) with moderate conversions and excellent selectivity toward corresponding aldehydes. Moreover, the reactivity trend of those substrates is 4-methyl >4-methoxy > H > 4-chloride, which is not related to the strength of the C−H bond of those substrates. We relate this to the different preadsorption of the substrate on the surface of catalyst,[23] which is significantly modified by the substitution. Detailed investigations in the adsorption effect induced by functional groups on the conversions of catalytic oxidation of various substituted substrates are still in progress.

Table 2. Selective Oxidation of Substituted Toluenes over mpg130.[a]



Substrate	t (h)				Con. (%)
	4	–	>99	–	2.5
	16	2	94	4	5.8
	4	–	>99	–	0.8
	16	–	>99	–	1.1
	4	–	>99	–	2.5
	16	–	>99	–	4.4

[a]Typical conditions: 10 mL of substrates, 500 mg of catalyst, O_2 (10 bar), 160 °C.

In any case, the current results reveal that highly porous mpg-C_3N_4 catalyst exhibits a high chemoselectivity and functional group tolerance for the oxidation of methyl groups, and therefore should be useful in overcoming the challenges of metal-mediated catalysis, which usually result in acids or esters.

As a good replacement for noble-metal catalysts, mpg-C_3N_4 also shows excellent stability and reusability. The catalyst was facilely recovered from the reaction solution via centrifugation or filtration, and reused for multiple circles, without obvious loss of its catalytic activity and selectivity (Entry 14−15, Table 1). The TON in terms of total amount of benzaldehyde transferred over mpg130 exceeded 20 after five circles of reuse (Supporting Information, Table S3), unambiguously indicating that the reaction indeed proceeds catalytically. After reaction, no obvious changes in the structure of framework of carbon nitride as demonstrated by the FTIR and XRD analysis (Supporting Information, Figure S3) and also the surface area (120−140 m^2/g) indicate much higher "real" TONs and speak for the excellent stability and reusability of g-C_3N_4 based catalysts.

To conclude, nanoporous mpg-C_3N_4 has been shown to be a mild, stable, and highly selective catalyst/moderator for the solvent-free oxidation of toluene and various derivates to corresponding aldehydes. The sustainable catalysts are relatively active in these catalytic oxidation reactions, even when compared to those of reported noble-metal catalysts. When the facile modification of carbon nitride based materials by engineering the composition and surface functional groups is considered, our results can be regarded as only a first step toward other functional carbon nitride nanocatalysts with improved or new activities.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, elemental analysis results, TEM images, XRD patterns, and FTIR spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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Funding

This work was supported by the L2H project of BMBF, the EnerChem project, the UNICAT project and the AvH Foundation.

Notes

The authors declare no competing financial interest.

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