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Fe-g-C_3N_4-Catalyzed Oxidation of Benzene to Phenol Using Hydrogen Peroxide and Visible Light

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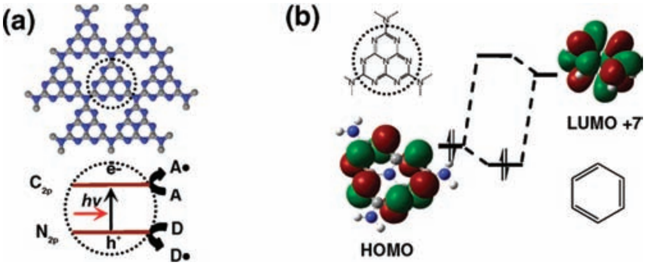
Direct oxidation of benzene to phenol with clean oxidants (e.g., O_2, H_2O_2) is an alternative to current phenol production based on the three-step cumene process.[1] Re/HZSM-5 and $H_7PMo_8V_4O_{40}$ were demonstrated to catalyze the aerobic oxidation of benzene to phenol in the presence of CO and NH_3, respectively, while titanium silicate (TS-1) zeolites were reported to activate H_2O_2 for a one-step phenol synthesis from benzene.[2] However, the introduction of an efficient process for the one-step phenol production remains one of the grand challenges of green synthesis as phenol is thermodynamically easier to oxidize than benzene. Selective transformation of benzene to phenol can be achieved in a Pd membrane reactor using H_2 and O_2.[3] Phase-transfer catalysis has also been developed, in which iron compounds, acids, and H_2O_2 were used as catalyst, cocatalyst, and oxidant, respectively. The optimized system was able to realize 8.6% benzene conversion with 97% selectivity (based on benzene).[4]

We recently studied the catalytic properties of porous graphitic carbon nitride (g-C_3N_4, Scheme 1a) and found that it was able to adsorb and activate benzene chemically (Scheme 1b) and, thus, catalyzed not only Friedel−Crafts reactions of benzene but also phenol synthesis using benzene and CO_2.[5] Interestingly, g-C_3N_4 was also found to be an all-organic solid photocatalyst with a semiconductor absorption setting at wavelengths of 460 nm.[6]

Scheme 1[a]



[a] (a) Stacked g-C_3N_4 sheets function as an all-organic solid-state photocatalyst promoting redox reactions with visible light. (b) Chemical interaction of benzene and defective g-C_3N_4 via HOMO−LUMO hybridization of melem and benzene.

It is shown in this paper that this is extendable to ~650 nm by iron complexation, thus resulting in a new bioinspired nonheme iron catalyst capable of activating H_2O_2 under mild conditions.[6c] This system features unique catalytic and photocatalytic properties together with additional binding functions imposed by the metal. Direct oxidation of benzene to phenol with H_2O_2 catalyzed by porous Fe-g-C_3N_4 is analyzed, in both the presence and absence of visible light irradiation.

First, the activity of bare mesoporous g-C_3N_4 (mpg-C_3N_4) without iron complexation was analyzed in a biphasic water-H_2O_2/acetonitrile medium in a stirred self-pressurized glass reactor. Phenol was formed with a very low turnover frequency (TOF = 0.008 h^{-1}), which can be enhanced to 0.16 h^{-1} under visible light irradiation ($\lambda > 420$ nm). A reference experiment in the absence of mpg-C_3N_4, but in the presence of hydrogen peroxide and visible light, revealed no measurable conversion (Table 1, entry 11). It is therefore evident that it is indeed mpg-C_3N_4 which can photocatalyze direct oxidation of benzene to phenol, however with rather low activity. The direct phenol synthesis by a metal-free organocatalyst at mild conditions (60 °C, 4 h) and especially at neutral pH is nevertheless a remarkable observation.

Table 1. Catalytic Activities for Phenol Production from Benzene by g-C_3N_4 Based Catalysts with(+)/without(−) Visible Light ($\lambda >$ 420 nm)[a]

entry	catalyst	*hv*	*t* (h)	benzene conv. (%)[b]	TOF × 100 (h^{-1})[c]
1	g-C_3N_4	−	4	0	-
2	g-C_3N_4	+	4	0	-
3	mpg-C_3N_4	−	4	0.1	0.8
4	mpg-C_3N_4	+	4	2.0	16.3
5	Fe-g-C_3N_4	−	4	1.8	16.1
6	Fe-g-C_3N_4	+	4	4.8	43.1
7	Fe-g-C_3N_4/SBA-15[d]	−	4	6.7	835.7
8	Fe-g-C_3N_4/SBA-15	+	4	11.9	1484.1
9	Fe/SBA-15	+	4	1.0	-
10	g-C_3N_4/SBA-15	+	4	0.1	14.8
11	-	+	10	0	-
12[e]	Fe-g-C_3N_4	+	4	0	-
13	$FeCl_3$	+	4	0.5	-

[a] Reaction conditions, see Supporting Information. [b] Moles of produced phenol/moles of initial benzene × 100. [c] Turnover frequency: *n* (phenol) per *n* (melem units) per hour. [d] The reaction was done using the 0.2-Fe-g-C_3N_4/SBA-15 catalyst. [e] 1 mL ethanol was added into the reaction system.

To improve the reactivity, transition metals can be applied to modify g-C_3N_4 photocatalysts. Metal doping to modify semiconductor properties is well-known for inorganic photocatalysts, e.g., TiO_2,[7] but effective modifiers for g-C_3N_4 catalysts for selective organic photosynthesis have not been reported yet. Indeed, modification with oxophilic Fe ions greatly enhanced the catalytic/photocatalytic activity of the system for oxidation of benzene to phenol. With 10 wt % Fe-modified g-C_3N_4 catalysts, the phenol yield based on benzene was 1.8% in the dark and 4.8% in visible light, and there was no detectable side product according to GC-MS in both cases, possibly due to the adsorption of some products on the catalyst or the formation of products such as tars which is not detected by GC. However, the phenol selectivity based on H_2O_2 was 3.2% in the dark and 8.3% in visible light (Table S1). Element analysis of the reactant mixture after the reaction reveals a small loss of Fe from the catalyst. The initial weight ratio of Fe:g-

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C_3N_4 was ~10% for the fresh sample, but it decreased to ~9.7% after the reactions. A control experiment using the leached Fe (Table 1, entry 13) revealed a benzene conversion of 0.5%, indicating that phenol synthesis by Fe-g-C_3N_4 was promoted primarily by heterogeneous catalysis. Optimization of preparation parameters leads to a 10 wt % Fe-amount of the carbon nitride polymer (Table S2). Iron was found to have the best promotional effect among the metals examined (Table S3). To test the catalytic stability, the used catalyst was washed, dried at 75 °C, and then re-examined with a new reactant mixture. The yield and selectivity of the three consecutive runs were virtually identical to those in the initial experiment with fresh Fe-g-C_3N_4 (Figure S1). There is no noticeable change in XPS spectra and iron redox potentials for the catalyst before and after the reaction, again reflecting the stability of catalyst (Figure S2 and S3). Both fresh and used samples showed electrocatalytical activities to reduce/oxidize H_2O_2.

It should be noted that the employed Fe-g-C_3N_4 is a bulk material and has only a low specific surface area (8 m^2/g). As heterogeneous catalysts should be improved with increasing surface area (note that the corresponding iron-free bulk g-C_3N_4, due to lack of surface sites cannot activate benzene; entries 1 and 2 of Table 1), it is desirable to generate porous Fe-g-C_3N_4. We thus coated SBA-15, a widely used mesoporous catalyst support, with nanometer thin Fe-g-C_3N_4 layers.

This was accomplished by loading dicyandiamide and $FeCl_3$ into the mesopore system of SBA-15, followed by copolymerization at 600 °C. The resulting materials were characterized with a variety of techniques. Low-angle XRD patterns showed that the mesostructure of SBA-15 remains after deposition of Fe-g-C_3N_4. The TEM images in Figure 1A confirmed the presence of a 2D hexagonal network, and no aggregated species was observed. This result, together with the elemental mapping images (in Figure 1A), indicates homogeneous coating of Fe-g-C_3N_4 on the SBA-15. The characterization results (Table S4, Figure S4, Figure S5, and Figure S7) also gave evidence that fully functional Fe-g-C_3N_4 was indeed applied onto the SBA-15 support.

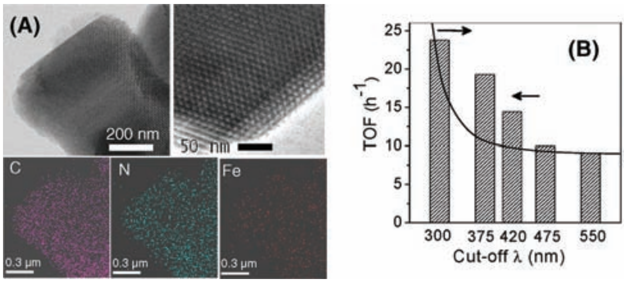

Figure 1. (A) Typical TEM images of Fe-g-C_3N_4/SBA-15 and corresponding elemental mapping images of C, N, and Fe. (B) Wavelength dependence of the phenol production rate on Fe-g-C_3N_4/SBA-15.

The activity of Fe-g-C_3N_4/SBA-15 for the oxidation of benzene to phenol is also listed in Table 1. Even in the dark, the phenol yield reached 6.7%, with a TOF = 8.36 h^{-1}. This is ca. 50 times faster than the corresponding bulk material (TOF = 0.16 h^{-1}) and approximately proportional to the increase in specific surface area. Visible light irradiation ($\lambda > 420$ nm) of the system can further improve the yield to ~12%, the TOF to 14.84 h^{-1}, respectively. The phenol selectivity based on H_2O_2 is also increased to 20.7% with visible light. These results demonstrate that the activity is related to the exposure of the Fe-g-C_3N_4 surface structure, runs also in the dark, but can be accelerated by coupling with photoredox catalysis.

To confirm the light-acceleration effect, we have tested the dependence of TOF on the wavelength of the incident light. The improved activity of Fe-g-C_3N_4/SBA-15 corresponds well with the UV/vis diffuse reflectance spectrum (Figure 1B). No enhancement was observed when the wavelength is >550 nm.

Classical Fenton's reagent (Fe^{2+}-H_2O_2) has been known for over 100 years for oxidation of benzene to phenol, but the Fenton oxidation systems were homogeneous and depended strongly on the presence of strong acids (e.g., CF_3COOH, $HClO_4$, H_2SO_4),[4,8] giving rise to processing problems during post-treatment. The present system is obviously free of acid and, as a solid, separable and recyclable.

The nature of the active species for reaction systems containing iron complexes and H_2O_2 was further investigated. Light-illuminated Pt/g-C_3N_4 is able to reduce water to hydrogen (evolution rate: 18 µmol/h);[6b] however, for Pt/Fe-g-C_3N_4, no hydrogen was observed under the same conditions. This result suggests that the surface-bound Fe^{3+} (-Fe^{3+}) captures the photoinduced electrons. This is supported by electrochemistry: The reduction potential of Fe^{3+}-g-C_3N_4/Fe^{2+}-g-C_3N_4 was measured to be +0.40 V vs NHE (Figure S3a), which is more positive than $E^0_{red}(H^+/H_2) = 0$ V. The resulting -Fe^{2+} is able to bind and reduce H_2O_2 to produce •OH. The presence of •OH could also be experimentally proven (Figure S8). We also tried to perform phenol synthesis in the presence of ethanol (a well-known reagent for capturing •OH),[9] and no phenol was observed. These results strongly suggest that the reaction progresses via •OH-radicals. Nevertheless, future work will have to focus on the examination of surface ferryl species on the catalyst when it reacts with H_2O_2.

In summary, we have shown that Fe-g-C_3N_4 is active for the direct oxidation of benzene to phenol using hydrogen peroxide. By taking advantage of the photocatalytic functions of g-C_3N_4, the yield of the phenol synthesis can be markedly improved. Work along improving the catalyst performance by synthesizing a real mesoporous, nonsupported Fe-g-C_3N_4 is ongoing. We assume that this new solid-state iron-based catalyst with semiconductor functions in combination with a high surface area holds great promise for oxidation reactions in synthetic chemistry in general: it nicely combines photocatalysis with metal-free organosynthesis.

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Supporting Information Available: Experimental details and more characterization and reaction results. This material is available free of charge via the Internet at http://pubs.acs.org.

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