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Metal-Free and Solvent-Free Oxidative Coupling of Amines to Imines with Mesoporous Carbon from Macrocyclic Compounds

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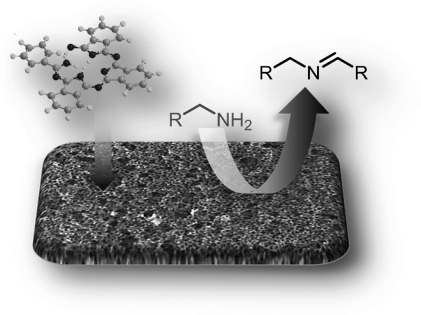
Ⓢ *Supporting Information*

ABSTRACT: A new series of carbon-based heterogeneous catalysts aiming at the oxidative coupling of amines to imines is disclosed here, which are easily synthesized by pyrolysis of macrocyclic compounds, including phthalocyanine and porphyrin under different temperatures. Silica colloid or ordered mesoporous silica SBA-15 is employed as the hard template to fulfill the mesoporous structures. The most active catalyst fabricated from phthalocyanine and silica colloid shows remarkable catalytic activity, excellent selectivity, and robust stability toward the imine formation in the presence of molecular oxygen under neat conditions. Kinetic analysis demonstrates that the apparent activation for benzylamine oxidation is 47.6 kJ mol^{-1} and that cationic species are involved in the reaction. The unprecedented performance of mesoporous carbon catalysts can be attributed to their high surface area, profitable pore volume, as well as homogeneous distribution of defect sites.



KEYWORDS: *imines, aerobic oxidation, heterogeneous catalysis, metal-free, mesoporous carbon*

1. INTRODUCTION

Imines and their derivatives are among the most important and valuable building blocks for a variety of fine chemicals,[1] pharmaceuticals,[2] and molecular motors.[3] Among the reported strategies for the imine fabrication,[4] the oxidative coupling of amines provides an attractive alternative to the conventional synthetic protocols, which often require unstable aldehydes and acid catalysts.[5] Although significant progress has been made for this coupling reaction during the past decade,[6] key challenges still exist, as follows: the intermediates generated from amines may rapidly dehydrogenate into nitriles' byproducts and result in poor selectivity;[5b,7] the involvement of an organic solvent makes the separation and purification of unstable imines very difficult and also brings environmental issues. Furthermore, the mainly reported catalytic systems were based on metal catalysts, such as Au,[8] Pd,[9] Ru,[10] V,[11] Cu,[12] and Fe.[13] Undoubtedly, the presence of metal incurs cost problems and metal contaminants in the final products, particularly for the pharmaceutical reagents. Therefore, the development of highly selective and cost-effective heterogeneous metal-free catalysts for the oxidative coupling of amines under solvent-free conditions is highly desirable.

Recently, mesoporous carbon materials have shown great potential as sustainable catalysts for organic synthesis.[14] The outstanding catalytic behaviors of these materials are related to the high surface area and pore volume,[15] the facile physical and chemical modification of the surface,[16] and the tunable electron features by doping with other elements (such as B, N, S, P).[17] Although fewer carbon-based catalysts have been currently developed for the oxidative coupling of amines,[18] limitations that hinder the practical application of these catalysts are remaining. For example, the graphene oxide presented by Huang[18a] suffers from the tedious preparation and high catalyst loading (50 wt %). The boron- and nitrogen-codoped hoely graphene reported by Li[18d] has the drawback of great consumption of the volatile precursor. Besides, addition of external hetroatom-containing molecule into the carbon source is not an effective way to obtain heteroatom doped carbon catalysts.

Inspired by the achievements of electro-catalyst derived from macrocyclic compounds and the advantages of these compounds with a relatively high thermal stability as well as molecular-level containing C and N elements.[19] Herein, we select phthalocyanine or porphyrin as a precursor and silica as a hard template to prepare the mesoporous carbon materials which, for the first time, exhibit high catalytic activity toward the oxidative coupling of amines. Various amines are smoothly transformed into the desired imines in high yields (up to 99%) with molecular O_2 as oxidant under neat conditions. Furthermore, the catalyst is easily recycled and retains excellent activity in a 100 mmol scale test with 0.47 wt % catalyst loading. Additionally, the relationship between the physicochemical property and catalytic behavior of the catalysts is discussed.

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2. EXPERIMENTAL SECTION

2.1. General. All chemicals were purchased from commercial sources and used without further purification. Products were confirmed by GC-MS (Agilent 7890A GC/5973 MS, SE-54 capillary column) and GC calculations of yields were performed on Agilent 7890A (SE-30 capillary column, FID detector) using N_2 as carrier gas.

2.2. Synthesis of Mesoporous Carbon Catalysts. Briefly, 2.5 g of silica colloid (Ludox HS-40, 40 wt % suspension in H_2O) was dispersed in a mixture of ethanol and chloroform (v/v = 3:1) under vigorous stirring. Then 1 g of phthalocyanine was added, and the whole mixture was stirred at room temperature for 1 h. After evaporation of the solvent at 90 °C, the obtained phthalocyanine/silica colloid was pyrolyzed at 800 °C (or 600, 700, 900 °C, ramp rate: 5 °C min^{-1}) for 2 h under flowing nitrogen and then cooled naturally to room temperature. The obtained powders were treated with 10 wt % hydrofluoric acid for 12 h, and this procedure was repeated once for removing the silicon template completely. Finally, the powders were thoroughly washed to neutral with water and dried in vacuum at 100 °C overnight. The mesoporous carbon materials were donated as Pc-Ludox-*X* (Pc was the abbreviation of phthalocyanine, Ludox represented the Ludox HS-40 silica colloid, and X referred to the carbonization temperature).

2.3. Procedures for the Oxidative Coupling of Amines. In a typical oxidation, 20 mg of catalyst and 5 mmol of benzylamine were introduced into a 10 mL Schlenk tube with a magnetic bar. The tube was vacuumed and purged with oxygen three times before it was finally connected with an oxygen balloon. Subsequently, the tube was stirred at the desired temperature. After completion of the reaction, the catalyst was separated by centrifugation. Both 250 mg of internal standard (biphenyl) and 12 mL of CH_3CN were added. The crude mixtures' analyses were performed on GC and confirmed by GC-MS.

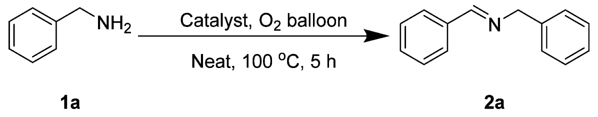
2.4. Large-Scale and Recycling Test. The reaction was conducted in a 100 mL autoclave equipped with a pressure control system, and 50 mg of catalyst and 100 mmol of benzylamine were added into the autoclave. The autoclave was sealed, purged with O_2 to exclude the air three times, charged the O_2 pressure to 0.5 MPa, and kept constant during the reaction. Then, the reaction was stirred at 120 °C for 24 h. The liquid reaction mixtures were analyzed by GC and confirmed by GC-MS. The catalyst was filtered and washed thoroughly with ethanol. Finally, the recovered catalyst was dried under vacuum at 100 °C overnight and reused in the subsequent recycling reaction.

2.5. Instruments. N_2 sorption isotherms were measured at 77K using a QuadraSorb SI4 Station, and the samples were degassed at 300 °C for 6 h before the measurements. Scanning electron microscope (SEM) images were conducted on a JSM-7800F microscope operating at an acceleration voltage of 20 kV. Transmission electron microscope (TEM) images were acquired with JEM-2100 microscope. Surface compositions were determined by X-ray photoelectron spectroscopy (XPS) using Thermo Scientific ESCALAB 250Xi instrument with Al Kα radiation anode ($h\nu$ =1486.6 eV), and the C 1s line (284.6 eV) was used as the reference to correct the binding energies (BE).

3. RESULTS AND DISCUSSION

To explore the activity of the prepared mesoporous carbon catalysts in the oxidative coupling of amines, solvent-free oxidation of benzylamine (**1a**) with O_2 balloon, which often employed the precious metal catalysts, was chosen as the model reaction. No product was detected in the absence of catalyst at 100 °C (Table 1, entry 1). Interestingly, performing the reaction with the commercially available phthalocyanine resulted in 20% conversion with 97% selectivity (Table 1, entry 2). To our delight, the mesoporous carbon catalysts derived from phthalocyanine showed high activity and excellent selectivity toward the reaction, and Pc-Ludox-8 exhibited the highest efficiency affording the desired imine in 90% yield (Table 1, entries 3−6). Upon employing SBA15 instead of Ludox as the template, the yield was decreased to 75% (Table 1, entry 7). Notably, direct carbonization of phthalocyanine without any template led to an inactive catalyst (Table 1, entry 8). Besides, when tetraphenylporphyrin (TPP) was chosen as the precursor, the catalyst also showed a moderate activity for the reaction (Table 1, entry 9). For comparison, mesoporous graphitic carbon nitride (mpg-C_3N_4) in our case gave 18% yield (Table 1, entry 10). Subsequently, the reaction conditions were investigated. Whether the reaction was conducted at 80 °C or in air balloon, the conversion of **1** was gradually decreased (Table 1, entries 12−13). Once the reaction was performed in nitrogen atmosphere, only 4% yield of the desired product was obtained (Table 1, entry 14), ensuring that O_2 as oxidant was essential for the reaction.

Table 1. Oxidative Coupling of Benzylamine Promoted by Different Catalysts[a]



entry	catalyst	conversion [%][b]	selectivity [%][b]
1	-	-	-
2	Pc	20.6	97.1
3	Pc-Ludox-6	53.6	95.9
4	Pc-Ludox-7	75.3	99.9
5	Pc-Ludox-8	90.9	99.1
6	Pc-Ludox-9	89.6	98.4
7	Pc-SBA15-8	77.3	96.5
8	Pc-8	3.5	97.2
9	TPP-Ludox-8	55.4	99.8
10	mpg-C_3N_4	19.5	96.4
11[c]	Pc-Ludox-8	63.8	99.5
12[d]	Pc-Ludox-8	32.3	97.2
13[e]	Pc-Ludox-8	4.1	97.5

[a] Reaction conditions: **1a** (5 mmol), catalyst (20 mg), O_2 balloon, 5 h, 100 °C. [b] Determined by GC using diphenyl as the internal standard and confirmed by GC-MS. [c] 80 °C. [d] Air balloon. [e] N_2 balloon.

Encouraged by these promising results, we further tested the effectiveness and stability of the present system. A 100 mmol-scale synthesis of *N*-benzylidene benzylamine (**2a**) was performed on Pc-Ludox-8 to investigate its large-scale production under solventless conditions. As shown in Figure 1, the oxidative coupling reaction proceeded smoothly, and the corresponding **2a** was obtained in 95% yield. Besides, the catalyst can be easily recovered by filtration and reused at least five times without any obvious loss of activity on this 100 mmol

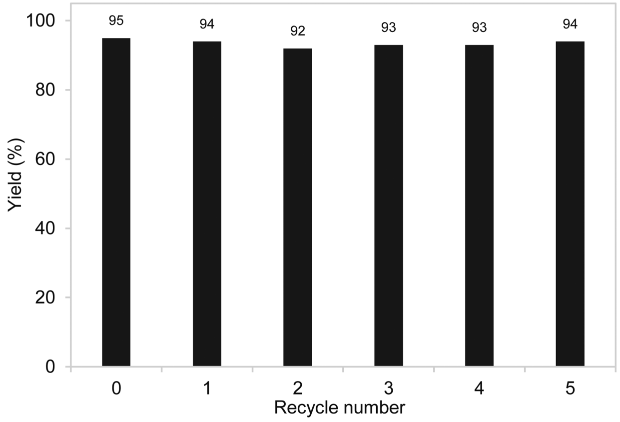


Figure 1. Pc-Ludox-8-catalyzed 100 mmol scale of the oxidative coupling of benzylamine. Reaction conditions: **1a** (100 mmol), catalyst (50 mg), 0.5 MPa O_2, 24 h, 120 °C. Yields were determined by GC.

scale experiment. Note that the catalyst loading here was only about 0.47 wt % and was one magnitude lower than that of reported carbocatalysts.[18]

Representative scanning electron microscopy (SEM) micrograph for Pc-Ludox-8 was displayed in Figure 2a, clearly indicating the introduction of pore structures into the resulting carbons. Further detailed structural information was obtained by transmission electron microscopy (TEM). As shown in Figure 2b, the interconnected vesicle-like frameworks of the catalyst were obvious, and the pore sizes had a range from several to dozens of nanometers. The selected-area electron diffraction (SAED) image revealed the multicrystalline structure of the sample (Figure 2c). Large-scale elementals mapping analysis demonstrated the uniform distribution of C, N, O and excluded the possible presence of other elements (Figure 2d). Well-defined linear array of mesoporous structure was observed for Pc-SBA15−8 (Figure 2e), reflecting that the structure of SBA-15 was successfully transferred into the catalyst. For comparison, bulk aggregations were presented in Pc-8 prepared without using any template, and the smooth surface implied their poor porosity (Figure 2f). Therefore, the catalysts with discrepant morphologies were prepared via different templates under the same pyrolysis temperature and presented significantly different activities toward the oxidative coupling of amines. Thus, it was deduced that the microstructure of the catalysts played important roles in the reaction.

To unveil the underlying factors affecting the catalytic activity, the microstructure of the catalysts were analyzed by N_2 sorption (Figure 3). The isotherms of Pc-Ludox-8 displayed an IUPAC type-IV curve and H4-type hysteresis loop, suggesting the mesoporous nature of the catalyst. The Brunauer−Emmett−Teller (BET) surface area and pore volume were 751 m^2/g and 2.2 m^2/g, respectively. A broad pore size distribution of Pc-Ludox-8 was presented in the entire testing range (3−60 nm), and the major pore size was centered at 17

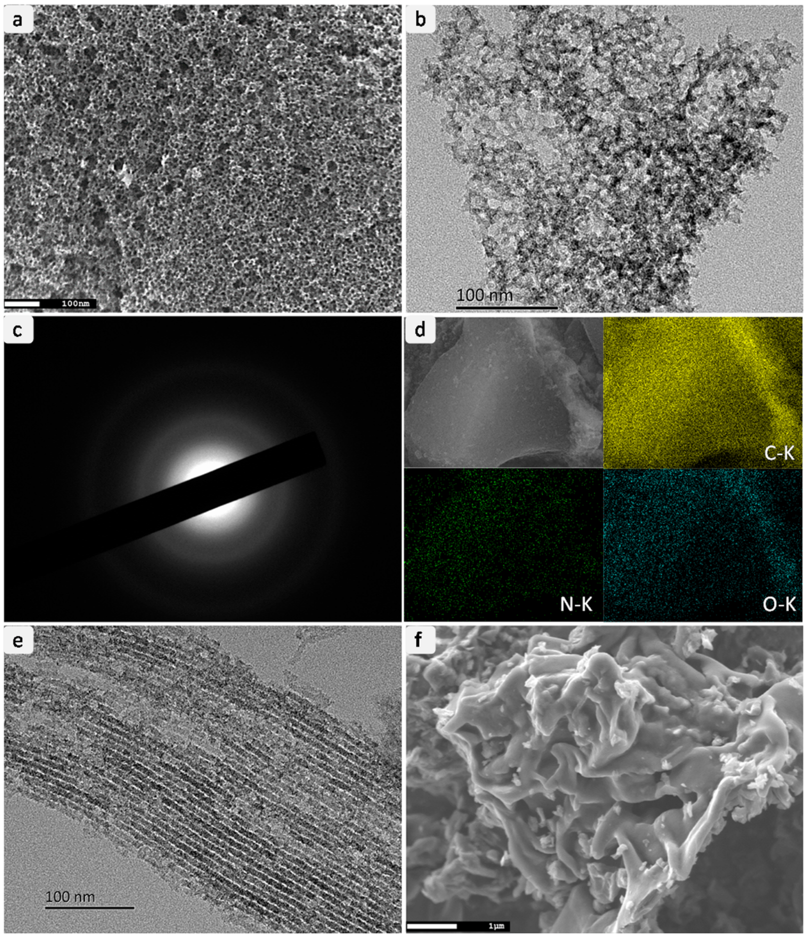


Figure 2. (a) SEM image, (b) TEM image, (c) selected area electron diffraction (SAED) pattern of the edge area, and (d) large-area SEM image along with the corresponding C-Ka, N-Ka, and O-Ka elemental maps of Pc-Ludox-8; (e) TEM image of Pc-SBA15−8; (f) SEM image of Pc-8.

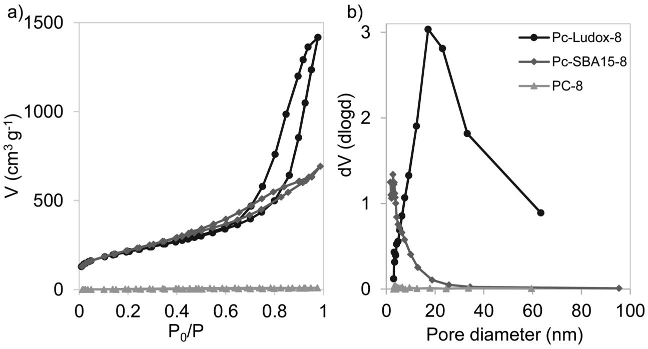


Figure 3. (a) N_2 sorption isotherms and (b) the corresponding BJH pore size distribution plots of Pc-Ludox-8, Pc-SBA15-8, and Pc-8.

nm according to the Barrett–Joyner–Halenda (BJH) model. Similarly, Pc-SBA15-8 also exhibited a type-IV sorption isotherm with a weak type H4 hysteresis loop. The BET surface area was up to 789 m^2/g, whereas the corresponding pore volume and the major pore size were 1.0 m^2/g and 2.7 nm, respectively, much smaller than that of Pc-Ludox-8. In contrast, no evident mesopore was detected for Pc-8. This structural information was consistent with the SEM and TEM observations (Figure 2 and Figure S4). It was widely accepted that the catalyst with a high surface area and pore volume was beneficial for mass transfer and exposure of more catalytic active sites, which played important roles in promoting the reaction activity.[20] Although the surface area of Pc-Ludox-8 was slightly lower than Pc-SBA15-8, the advantages of pore volume and pore size might assist it to gain a better performance. From this perspective, the Pc-8 showed low activity toward the reaction was reasonable.

In spite of similar pore structures and surface areas (Table 2), the Pc-Ludox-*X* (*X* = 6, 7, 8, 9) presented different reaction activities toward the amine oxidation. Thus, it was necessary to discuss the relationship between their components and the activities. The element components of the samples were determined by X-ray photoemission spectroscopy (XPS) analysis. The contents of nitrogen were reduced from 8.5 to 5.1 atom % as the pyrolysis temperature increased from 600 to 900 °C, indicating a high degree of agglomeration was obtained and more nitrogen atoms were incorporated into the carbon matrix. The high-resolution N 1s spectra of Pc-Ludox-8 and other samples can be fitted with four peaks, including pyridinic N (398.1 eV), pyrrolic N (399.6 eV), graphitic N (400.7 eV), and pyridine N oxide (403.2 eV) (Figure 4a). As the pyrolysis temperature increased to 900 °C, the contents of graphitic N increased while the contents of the pyridinic N decreased, suggesting graphitic N was more stable than pyridinic N, and the latter may be transformed into the former under higher temperature (Figure S7). Previous studies have shown that the introduction of nitrogen into the carbon-based catalyst can induce the electron relocalization to activate the oxygen molecules and substrates in oxidation reactions.[18d,e,21] Here, we might attribute the benefits to the increase of graphitic N species, which promoted the oxidative coupling of amines with molecular oxygen. In addition, a certain amount of oxygen implanted by the inorganic template was present in these catalysts,[22] which were divided into three peaks centered at 530.6, 532.2, and 533.8 eV (Figure 4b). According to the literature,[23] the peaks at 530.6 and 532.2 eV were assigned to the absorbed oxygen-containing components and C═O groups, respectively, whereas the peak at 533.8 eV belonged to the C−OH and/or C−O−O-H groups. It was noteworthy that the carboxylic acid groups with large π-conjugation system in graphene oxide played an important role in activation of the substrates.[18c] In order to evaluate the possible effects of these carboxylic acid groups, the Pc-Ludox-8 was treated with NaOH or $NaBH_4$, respectively. However, we did not observe any appreciable change in both activity and selectivity compared with the fresh Pc-Ludox-8 (Table S1). Therefore, the contribution of carboxylic acid groups to the reaction can be excluded. The C 1s spectrum of Pc-Ludox-8 were deconvoluted into four peaks centered at 284.6, 285.7, 286.5, and 288.0 eV (Figure 4c), corresponding to the C═C, C−N, C−O, and O−C═O groups, respectively.[23b] Furthermore, as the pyrolysis temperature raised from 600 to 900 °C, the contents of carbon increased from 87.4 to 89.7 atom % along with the reduction of N or O atoms linked directly to the C atoms (Table 2). As a result, more defect sites derived from the restacking of C atoms were originated, which can remarkably enhance the reaction activity. Previous works also proposed the mesoporous carbon catalysts owned more active sites for oxygen adsorption and activation than that of oxygen-inert mpg-C_3N_4,[24] which might explain why mpg-C_3N_4 showed low activity for the coupling of amines.

With the optimized conditions (Table 1, entry 5), the yield of **2a** can be further increased to 94% without loss of the selectivity by simply prolonging the reaction time to 5.5 h (Table 3, entry 1). Then, a series of amines with different substituted groups was tested, and the results are listed in Table 3. In general, benzylamines substituted with electron-donating groups (Me, OMe) or electron-withdrawing groups (F, Cl, Br, CF_3) were suitable substrates for the reaction, affording the corresponding imines in excellent yields. However, the electronic properties of the substituents on the phenyl ring have some effects on the efficiency of the reaction, the former (Table 3, entries 2−3) was more favored to be oxidized than the latter (Table 3, entries 6−9). Moreover, it was found that the reaction was sensitive to the steric hindrance of the substituents on the phenyl ring, and *para*-substituted amine exhibited a higher activity than *meta*- and *ortho*-substituted isomers (Table 3, entries 3−5). Note that heterocyclic amines, including 2-furfurylamine and 3-picolylamine, which might poison the metal catalyst due to the coordination with the metal active sites, could also be transformed into the

Table 2. Results of N_2 Sorption and Chemical Compositions of the Mesoporous Carbon Catalysts

sample	S_{BET} (m^2 g^{-1})	V_{Total} (cm^3 g^{-1})[a]	D_{Pore} (nm)[b]	C content (atom %)[c]	N content (atom %)[c]	O content (atom %)[c]
Pc-Ludox-6	726	1.7	12.4	87.4	8.5	4.0
Pc-Ludox-7	745	1.8	17.9	87.6	8.5	3.9
Pc-Ludox-8	751	2.2	17.1	88.1	6.9	4.9
Pc-Ludox-9	754	2.0	17.4	89.7	5.1	5.2

[a] Determined from the adsorption volume at $p/p_0 = 0.98$. [b] Calculated using the BJH method. [c] Measured by X-ray photoelectron spectroscopy.

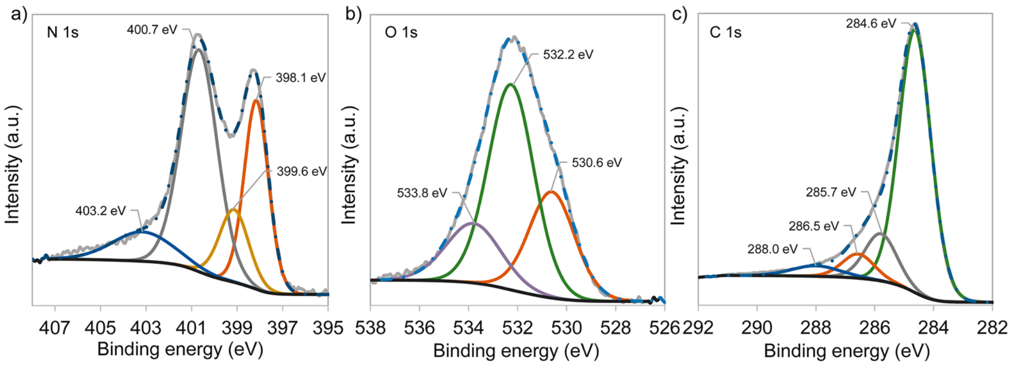
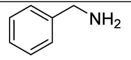
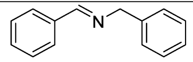
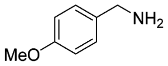
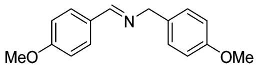
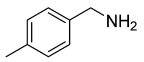
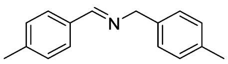
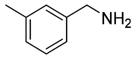
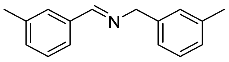
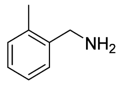
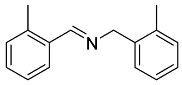
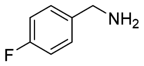
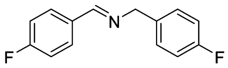
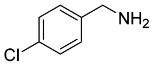
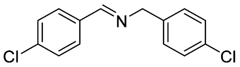
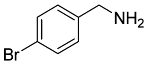
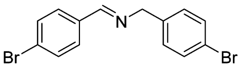
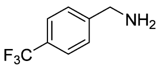
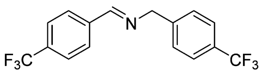
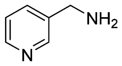
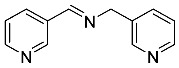
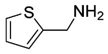
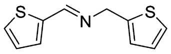
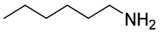
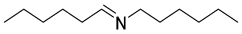
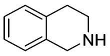
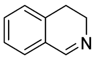


Figure 4. High-resolution XPS spectrum of Pc-Ludox-8 with the N 1s (a), O 1s (b), and C 1s (c).

Table 3. Oxidative Coupling of Various Amines to Imines over Pc-Ludox-8[a]

Entry	Substrates	Products	Time (h)	Yield [%][b]
1			5.5	94.2
2			5	94.3
3			5	91.2
4			8	98.2
5			8	95.1
6			6	99.4
7			6	99.0
8			6	99.6
9			6	90.3
10			6	72.0
11			4	84.4
12			12	13.1
13			18	73.4

[a]Reaction conditions: amines (5 mmol), catalyst (20 mg), O_2 balloon, 100 °C. [b]Determined by GC and confirmed by GC-MS.

corresponding imines in good yields (Table 3, entries 10−11). Attempts were made to oxidize the challenging aliphatic amines. Due to the inactive *a*-hydrogen of amine, a lower yield of the product was observed (Table 3, entry 12). Furthermore, the catalyst was also capable of selectively oxidizing 1,2,3,4-tetrahydroiso quinoline to give the corresponding imine in 73% yield (Table 3, entry 13).

To investigate the reaction performance with Pc-Ludox-8 in detail, the product evolution of the oxidative coupling of **1a** was supervised via continuous sampling by GC. As displayed in Figure 5a, the desired imine was the sole product during the whole of the reaction, and excellent selectivity was preserved even in the above 100 mmol scale experiment. The plot for the product can be well fitted with pseudo fist-order reaction kinetics in the range of 0 to 1 h, and the rate constant *k* was 0.3 h^{-1}. In addition, we did not observe an induction period at the start of the reaction, which was obvious in MOF-253 catalytic system.[25] The presentation of free-radical scavenger (BHT)

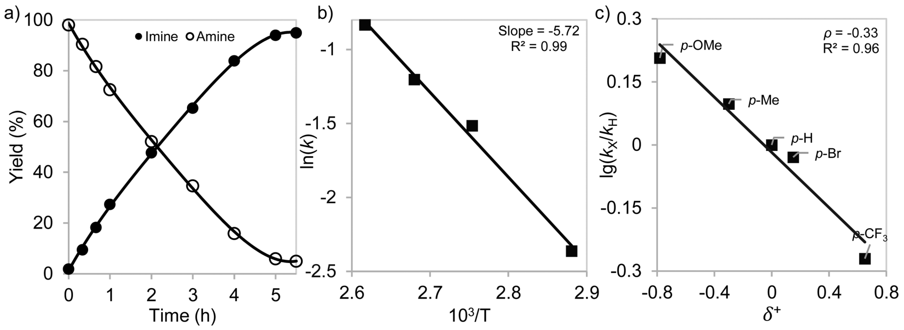
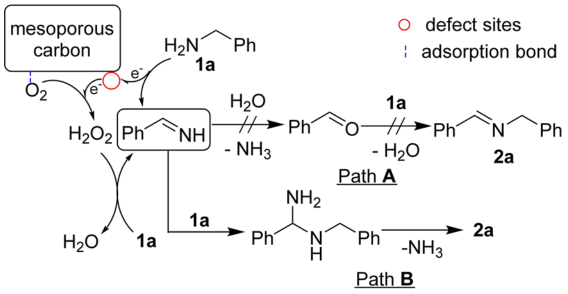


Figure 5. (a) Reaction profiles for the oxidative coupling of benzylamine over Pc-Ludox-8. (b) Arrhenius plot for the oxidation of benzylamine. (c) Hammet plot for the oxidative coupling of the *para*-substituted benzylamines, the lg(k_X/k_H) was obtained from the ratio of conversion with reaction time of 40 min.

was also failed to disturb the oxidation of **1a** (Table S1). Thus, we can exclude the possibility of a radical chain pathway for the reaction. The apparent activation for benzylamine oxidation E_a was calculated from the Arrhenius plot, and the value was 47.6 kJ mol^{-1} (Figure 5b), much smaller than the reported value of 62.8 kJ mol^{-1}.[26] Finally, the relative rates for the oxidative coupling of *para*-substituted benzylamines (CF_3, Br, H, Me, OMe) were investigated (Figure 5c). A reasonable linear relationship between log(k_X/k_H) and Brown−Okamoto constant σ^+ was established,[27] and the resulting reaction constant ρ was −0.3, indicating the intermediary of cationic species were involved in the reaction. The results in Table 3 were also proved that the reaction was substituent-sensitive, and the electron-donating substituents were more likely to be oxidized.

We further proposed the general reaction pathway for the synthesis of imines catalyzed by these mesoporous carbon catalysts (Scheme 1). In the initial phase of the reaction, both benzylamine and molecular oxygen were activated on the defect sites of catalysts and subsequently transformed into benzylimine and H_2O_2 intermediates, respectively. As the formation of H_2O_2 was not observed, we believed it reacted immediately with another molecular **1a** to obtain benzylimine.[18b,25] Given the unstable and easily decomposed properties, the generated benzylimine may readily transform as the following two pathway: (a) hydrolyzed to give the aldehyde, subsequently condensing with a second molecule of **1a** to produce the desired **2a**; (b) added with another molecule of **1a**, successively releasing NH_3 to give **2a**. In the Pc-Ludox-8-catalyzed solventless reaction described here, no signal of aldehyde was detected by GC-MS, and thus, we believed path **A** was unfavorable for the reaction. To test this hypothesis, *N*-benzylidenemethyl amine as the analogy of benzylimine was added to 1 equiv of **1a** with 20 mg of Pc-Ludox-8 (Scheme S1). 61% of *N*-benzylidene methylamine was transformed into **2a**, and the residual substrate can be recovered from the reaction mixtures. This observation strongly supported benzylimine was the intermediate, and the hydrolytic process to generate the aldehyde was unfavorable for the reaction. Based on the results *vide supra*, the oxidative coupling of amines in the present study proceeded via the path **B**.

Scheme 1. Proposed Reaction Pathways for Pc-Ludox-8-Catalyzed Oxidative Coupling of Primary Amines to Imines



4. CONCLUSION

In summary, we have developed a novel and metal-free carbon-based catalyst for the imine formation under solvent-free conditions. The mesoporous carbon materials are prepared by simple thermolysis of macrocyclic compounds such as phthalocyanine or porphyrin with silica templates. Applying these catalysts in the oxidative coupling of amines, it affords the corresponding imines in good to excellent yields with molecular O_2 as oxidant. Besides, the catalysts show potential performance in large-scale production and can be recycled several times without loss of the catalytic efficiency. It is revealed that the template and pyrolysis temperature influence the microstructure and surface compositions of the materials, respectively, and further affect the behaviors of the catalysts. More detailed studies are currently in progress in order to clarify other factors that determine the catalytic reactivity as well as the extensions of these catalysts to other oxidation reactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00244.

Additional preparation of materials, characterizations for mesoporous carbon materials, and controlled experiments (PDF)

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Notes

The authors declare no competing financial interest.

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