Synthesis of Nitrogen-Doped Mesoporous Carbon for the Catalytic Oxidation of Ethylbenzene

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Abstract. Nitrogen-doped ordered mesoporous carbon (NOMC) was fabricated via a simple hard-template method by functionalized ionic liquids as carbon and nitrogen source, SBA-15 as a hard-template. The obtained NOMC materials have a high nitrogen content of 5.55 %, a high surface area of 446.2 m2 g-1, and an excellent performance in catalysing oxidation of ethylbenzene. The conversion rate of ethylbenzene can be up to 84.5% and the yield of acetophenone can be up to 69.9%, the results indicated that the NOMC materials have a faster catalytic rate and a higher production of acetophenone than catalyst-free and CMK-3, due to their uniform pore size, high surface area and rich active sites in the carbon pore walls.

1. Introduction

Owing to various pore structures, high specific surface area and pore volume, mesoporous materials can be extensively used in many fields, such as purification of gases or liquids, separation of mixture, catalysis, etc. [1, 2, and 3]. With the continuous development of mesoporous carbon, mesoporous carbon materials are also capable of being utilized in a number of new filed, like flammable gas storage (hydrogen, methane), electric energy storage (supercapacitor) [4, 5]. The widely extended application areas make porous carbon have special properties, such as pore structures, surface chemical properties, crystalline order and morphologies [6, 7]. The surface chemical properties and morphologies of materials are crucial for numerous fields. Hence, preparation of highly ordered mesoporous carbon materials is the key point of many researches. In this sense, Nano casting is a very effective method for preparing ordered mesoporous materials and hard-template method is one of the typical synthetic approaches: the pores of crystalline inorganic solids (like zeolites, ordered mesoporous silica) as template are infiltrated by carbon precursors, the ordered mesoporous carbon can be obtained after carbonization to remove template [8]. As a result, carbon materials with different structures and morphologies can be made on the basis of different templates. Because SBA-15 possesses comparatively high surface area are, large pore volume, uniform pore size as well as good hydrothermal stability among masses of templates, it is often applied to prepare carbon materials [9]. By using SBA-15 as hard-template and glycerin as carbon source, M. Ignaz and co-workers tuned the infiltration amount of glycerin and successfully prepared highly ordered mesoporous carbon.

However, due to the amorphous silica framework of SBA-15, the chemical activity is similar to common silica and framework is liable to collapse during high-temperature crystallization, leading to low catalytic and ion exchange capacity. In order to overcome the deficiency of carbon materials, researchers have done a large number of works to change the surface chemical properties and
introduce active components. For example, introducing heteroatoms like nitrogen or boron into mesoporous carbon to replace part of carbon element can hugely change the surface structures and pore structures, enhance the hydrophilicity, affect the surface acid-base properties and provide massive active sites. The N- or B-doped porous carbon materials exhibited good performances in adsorption and catalytic reactions [8, 9]. The nitrogen doping method can be classified into in-situ doping and post processing method, and the common nitrogen sources include melamine resin, polyacrylonitrile, double acrylic amine, polyaniline, etc [10, 11, and 12]. Zhang and co-workers synthesized ordered mesoporous carbon in two-step method by using SBA-15 as hard-template, sucrose and polyaniline as carbon source and nitrogen source respectively. Because of the high nitrogen content, the product showed an excellent performance in electrochemical field, the capacitance reached 225 F g⁻¹ and maintained at 95% after 2000 cycles [13]. However, conventional carbon and nitrogen precursors are detrimental to environment and residual amount is quite low. Therefore, an environmentally benign precursor with high residual amount is urgent to be developed. Ionic liquids (ILs) can be proper candidates as carbon precursors on account of the low vapour pressure, low fusion temperature and high residual carbon amount. Another significant reason is that ILs contain heteroatoms, which is equivalent to direct doping [14, 15]. Liu and co-workers have prepared N-doped mesoporous carbon utilizing SBA-15 as template, functionalized ILs as nitrogen source, exhibiting great catalytic effect in cyclization reactions [16].

Herein, we report a facile approach to synthesize N-containing ordered mesoporous carbon by using SBA-15 as hard-template and functionalized ILs as carbon and nitrogen source. The pore size of nitrogen-containing mesoporous carbon via reverse replicating SBA-15 is 3.7 nm. A series of characterizations, including SEM, XPS and XRD show the product possesses bamboo-like structure, the nitrogen content is around 5.55%. Such material demonstrates obvious catalytic activity in ethylbenzene oxidation compared with CMK-3.

2. Experimental Section.

2.1 Preparation of mesoporous silica (SBA-15).
Mesoporous silica (SBA-15) was prepared by using triblock copolymer Pluronic P123 as template, tetraethyl orthosilicate (TEOS) as silicon source. For a typical synthesis, water, hydrochloric acid (HCl) and P123 were added into a beaker. The mixed solution was stirred at 50 °C for 30 min. After P123 was entirely dissolved, TEOS was added dropwise under vigorous stirring. Then the solution was kept stirring for 24 h. After that, the as-prepared solution was transferred into an autoclave. Hydrothermal treatment was then carried out in an oven at 100 °C for 24 h. The white powder was obtained after filtered, washed and dried in oven. Finally, the mesoporous silica (SBA-15) was obtained after calcination at 550 °C in air for 5 h (heating rate 1 °C min⁻¹) to remove organic components. The reaction system possesses a molar ratio for TEOS/P123/HCl/H₂O of 1:0.017:6:138.

2.2 Preparation of nitrogen-containing ordered mesoporous carbon (NOMC).
Component A: 1.88 g (0.02 mol) of 1-vinyl imidazole and 2.18 g of ethyl bromide were added into 20 ml of methanol. After reaction at 40 °C under nitrogen for 24 h, the product was evaporated and dried to a constant weight in a vacuum oven.

Component B: 1 g of SBA-15 was dissolved in ethanol solution, which is followed by adding 0.03 g of azodisobutyronitrile, 3 ml of N, N-dimethylformamide and 0.07 g of nickel nitrate. The mixed solution was stirred under room temperature until ethanol was completely evaporated.

Component B was added into component A and ethanol was added to form a clear solution. Then, the reaction was carried out at 60 °C under nitrogen for 6 h. The product was evaporated, dried to a constant weight in oven and transferred into tube furnace, calcined at 600 °C under nitrogen atmosphere for 3 h. The NOMC was finally obtained after etching silica template and washed with acid to remove nickel.
2.3 Characterization.
Wide angle X-ray diffraction (XRD) patterns and Small angle X-ray diffraction patterns were collected using a Rigaku D/MAX 2550 diffract meter (Cu K radiation, $\lambda = 0.15406$ nm), operated at 40 kV and 40 mA. The d-spacing values were calculated by the formula $d = 2\pi/q$. Scanning electron microscopy (SEM) images were taken on a Hitachi S-4800 microscope. Transmission electron microscopy (TEM) measurements were conducted on a JEM-2010 F microscope (JEOL, Japan). Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Tristar 3020 analyser. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area. The pore volumes and pore size distributions were obtained from the adsorption branches of isotherms by using Barrett-Joyner-Halenda (BJH) method, and the total pore volumes were estimated from the adsorbed amount at a relative pressure $P/P_0$ of 0.997. X-ray photoelectron spectroscopy (XPS) was recorded by using AXIS ULTRA DLD spectrometer with Al Ka radiation.

2.4 Catalytic measurement.
Ethylbenzene catalytic oxidation was operated in glass reactor under high pressure, equipped with thermostatic water bath, refluxing and magnetic stirring device. 10 mg of catalyst, 1 mol of ethylbenzene and 3 mol of tert-butyl hydro peroxide (TBHP) were added into 3 ml of water, the mixture was remained at 70 °C for 24 h. Then, 0.05 g of n-dodecanal and 6 ml of dichloromethane were added respectively for extraction. The content of mixture was measured by using Agilent GC 7820A.

3. Results and discussion.
The NOMC was synthesized by using ILs as nitrogen source and SBA-15 as hard-template. From Figure 1a, it can be seen that NOMC possesses bamboo-like morphology with uniform size, indicating NOMC is successfully copied from SBA-15. In Figure 1b, the length of NOMC is about 600–1000 nm, and aggregation or fragmentation is not observed in a large area. TEM images (Figure 1c and d) show that NOMC have intact ordered mesoporous without cracked parts, further demonstrating successful replication of pore structure of original template.

![Figure 1](image_url)

**Figure 1.** SEM images (a, b) and TEM images (c, d) of nitrogen-containing ordered mesoporous carbon (NOMC).

In Figure 2a, two peaks at 0.7 and 1.5 can be obviously observed, which can be indexed to (100) and (110) facets, respectively. The space structure matched with two-dimensional hexagonal mesostructured further confirms NOMC is replicated from silica template [11]. The wide-angle X-ray diffraction pattern (Figure 2b) reveals that two peaks at 23° and 44° correspond to (002) and (100) facets of graphite, indicating mesoporous carbon is graphitized to some extent [12]. The metal nickel is able to graphitize carbon at high temperature, resulting in graphitized structure after removal of SBA-15 and nickel [13].
Figure 2. (a) Small-angle X-ray diffraction (SAXS) and (b) Wide-angle X-ray diffraction (XRD) patterns of NOMC.

The nitrogen adsorption-desorption isotherms (Figure 3a) reveals characteristic type curves with distinguishable hysteresis loop at relative pressure $P/P_0 = 0.45-0.9$, reflecting the mesostructured of NOMC is well matched with TEM and XRD results [14, 15]. The pore size distribution calculated by Barrett-Joyner-Halenda (BJH) model is centered at 3.7 nm, which agrees well with wall thickness of SBA-15, indicating NOMC is templated from template SBA-15 [16]. The specific surface area and pore volume of NOMC are calculated to be 446.3 m$^2$/g and 0.77 cm$^3$/g, respectively.

Figure 3. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of NOMC.

The X-ray photoelectron spectroscopy (XPS) spectrum of N1s shows three peaks. The peak at 398.1 eV corresponds to sp2 hybrid bonds or pyridine-N in lamellar graphite. The peak at 400.3 eV is matched with pyrrole-N of nitrile functional groups linked with carbon. The peak at 401.4 eV belongs to graphite-N [11, 13, and 17]. The rearrangement of nitrogen atom during high temperature carbonization leads to insertion of N atom into carbon framework. The literature reported that graphite-N is capable of facilitating C-H activation. The XPS spectrum shows the surface content of NOMC is 5.55% and graphite-N is 27.6%, which benefits catalytic oxidation of ethylbenzene in liquid phase.

Figure 4. XPS core-level spectra of N 1s of NOMC.
In order to evaluate the catalytic performance of NOMC, we use NOMC as catalyst, tert-butyl hydro peroxide (TBHP) as oxidant to catalyze the oxidation of ethylbenzene in liquid phase. The yield of acetophenone and the conversion rate of ethylbenzene are used to evaluate the catalytic performance in this test (Table 1). The conversion rate and yield of acetyl benzene are 35% and 6% without any catalyst, revealing the autocatalysis of ethylbenzene. When CMK-3 is used as catalyst, the conversion rate and yield rise to 67.2% and 22.3%, showing mesoporous structure is favor to catalytic oxidation.

To further explore the impact factors of ethylbenzene oxidation, the catalytic abilities of CMK-3 and NOMC are carried on research. Table 1 shows the catalytic performance of NOMC (with conversion rate of 84.5% and yield of 69.9%) is far better than that of CMK-3. However, the surface area of CMK-3 is much higher than NOMC, indicating surface area of catalyst has little effect on oxidation of ethylbenzene, which is identical to report [18]. During the oxidation process of ethylbenzene to acetyl benzene, the N atom derived from NOMC is not directly involved in the catalytic reaction. Instead, N atom can change the electronic structure of adjacent C atom, and the graphite-N promotes C-H activation, resulting in considerable enhancement of catalytic performance.

### Table 1. Catalytic performance of ethylbenzene oxidation with different catalysts.

| Sample  | BET (m²/g) | Pore size (nm) | Pore volume (cm³/g) | N content (XPS) | Conversion rate (%) | Yield (%) | Reaction rate (μmol m⁻²h⁻¹) |
|---------|------------|----------------|---------------------|-----------------|---------------------|-----------|-----------------------------|
| No catalyst | /          | /              | /                   | /               | 35                  | 6         | /                           |
| NOMC    | 446.2      | 3.7            | 0.77                | 5.55            | 84.5                | 69.9      | 65.3                        |
| CMK-3   | 1271.7     | 3.6            | 0.58                | /               | 67.2                | 22.3      | 1.14                        |

### 4. Conclusion

Nitrogen-containing ordered mesoporous carbon (NOMC) was fabricated via a hard-template method by functionalized ionic liquids as carbon and nitrogen source, SBA-15 as hard-template and nickel nitrate as catalyst. NOMC samples have a high nitrogen content of 5.55 %, a high surface area of 446.2 m² g⁻¹ as well as uniform pore size, indicating NOMC was successfully replicated from template SBA-15 and ILs were impregnated into mesoporous. The conversion rate of ethylbenzene can be up to 84.5% and the yield of acetophenone can be up to 69.9%, which are far more than CMK-3. Besides, this work has extended the application fields of metal-free catalysts.

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### References

[1] Y.Y Li, K.K Han, W.G Lin, Fabrication of a new MgO/C sorbent for CO2 capture at elevated temperature, J Mater Chem A. 1 (2013) 12919–12925.
[2] Z.Z Xiao, F.F Peng, X.L Li, Surface modification of malonic acid-catalyzed carbon xerogels and their high performance for adsorption of Cu (II) ions, Surf Interface Anal. 45 (2013) 1869–1877.
[3] S Wang, W.C Li, G.P Hao, Temperature-Programmed Precise Control over the Sizes of Carbon Nanospheres Based on Benzoxazine Chemistry, J Am Chem Soc, 133 (2011) 15304–15307.
[4] Y Xiao, H.W Dong, C Long, Melaleuca bark based porous carbons for hydrogen storage,
International Journal of Hydrogen Energy. 39 (2014) 11661-11667.

[5] S.S Feng, W Li, J.X Wang, Hydrothermal synthesis of ordered mesoporous carbons from biomass-derived precursor for electrochemical capacitors, Nanoscale. 6 (2014) 14657-14661.

[6] Y Gu, Z.G Xiong, W.A Abdulla, A new approach to preparing porous carbons with controllable pore structure and morphology, Chem Comm. 50 (2014) 14824-14827.

[7] H.N Wang, X Rong, Han L, Controlled synthesis of hexagonal mesostructured silica and macroporous ordered siliceous foams for VOCs adsorption, RSC Adv. 5 (2015) 5695–5703.

[8] T Kyotani, Z Ma, A Tomita. Template synthesis of novel porous carbons using various types of zeolites, Carbon. 41 (2013) 1451–1459.

[9] M Ignat, C.J Van Oers, J Vernimmen, Textural property tuning of ordered mesoporous carbon obtained by glycerol conversion using SBA-15 silica as template, Carbon. 48 (2010) 1609–1618.

[10] J Wei, D.D Zhou, Z.K Sun, A Controllable Synthesis of Rich Nitrogen-Doped Ordered Mesoporous Carbon for CO2 Capture and Supercapacitors, Adv Funct Mater. 23 (2013) 2322–2328.

[11] J Wang, H.Y Liu, X.M Gu, Synthesis of nitrogen-containing ordered mesoporous carbon as a metal-free catalyst for selective oxidation of ethylbenzene, Chem Comm. 50 (2014) 9182-9184.

[12] M Li, J.M Xue. Integrated Synthesis of Nitrogen-Doped Mesoporous Carbon from Melamine Resins with Superior Performance in Supercapacitors, J Phys Chem C. 118 (2014) 2507-2517.

[13] N.N Liu, L.W Yin, C.X Wang, Adjusting the texture and nitrogen content of ordered mesoporous nitrogen-doped carbon materials prepared using SBA-15 silica as a template, Carbon. 48 (2010) 3579–3591.

[14] J.P Paraknowitsch, J Zhang, D.S Su, Ionic Liquids as Precursors for Nitrogen-Doped Graphitic Carbon, Adv Mater. 22 (2010) 87–92.

[15] J.P Paraknowitsch, A Thomas, M Antonietti, A detailed view on the polycondensation of ionic liquid monomers towards nitrogen doped carbon materials, J Mater Chem. 20 (2010) 6746–6758.

[16] Y Liu, J.J Peng, S.R Zhai, Synthesis of Ionic Liquid Functionalized SBA-15 Mesoporous Materials as Heterogeneous Catalyst toward Knoevenagel Condensation under Solvent-Free Conditions, Eur J Inorg Chem. 15 (2006) 2947–2949.

[17] Y.T Hu, H.J Liu, Q.Q Ke, Effects of nitrogen doping on supercapacitor performance of a mesoporous carbon electrode produced by a hydrothermal soft-templating process, J Mater Chem A. 2 (2014) 11753-11758.

[18] J Wang, H.Y Liu, X.M Gu, Synthesis of nitrogen-containing ordered mesoporous carbon as a metal-free catalyst for selective oxidation of ethylbenzene, Chem Commun. 50 (2014) 9182-9184.