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Study on synthesis of mesoporous carbon from MOF-199 metal-organic framework as potential adsorbent

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ABSTRACT

Porous carbon material is one of the most common and very important for various applications thank to its high surface area and adsorption capability. In this study, mesoporous carbon was prepared by thermal decomposition of copper-based metal-organic framework MOF-199 under inert atmosphere and followed by immersing in diluted HNO_3 solution in order to remove metal/metal oxide and activation of the resultant porous carbon. Scanning electron microscopy (SEM) revealed that as-prepared material remained intact octahedral morphology of pre-pyrolysis MOF structure, and product has spongy structure with specific surface area of 375 m^2/g as measured using N_2 adsorption isotherm (BET), which can be employed as an effective adsorbent.

Introduction

Metal-organic frameworks (MOFs) are emerging as a new kind of crystalline porous materials and have been extensively researched in laboratory scale for gas storage and separation [1], catalysis [2], drug delivery [3], etc. due to their tunable framework structures as well as adjustable pore size. However, their industrial application was limited because they are relatively unstable to chemical attack, some even lose its structure and porosity in aqueous media [4], not to mention most of them contain substantial amount of toxic heavy metals.

Many developments have been made in carbon technology recent years, especially as adsorbent in water treatment, including graphene [5], carbon nanotube [6], carbon quantum dots [7], etc. Among them, mesoporous carbon with high surface area are indispensable in many modern-day fields and are getting more and more attention from scientists. Traditional porous carbon materials are fabricated by heat treatment followed by activation of organic substances, like coconut shell, cotton, or synthetic polymers which often used as unselective adsorbent because of their inhomogeneous pore sizes. Recently, direct carbonization of MOFs has been demonstrated to be a facile route to synthesize porous carbon materials with high surface area (217 m^2/g) using MOF-5 [8]. Mesoporous carbon synthesized from MIL-53(Fe) by this method can also be used in advanced applications as drug delivery because of its high surface area (200 m^2/g) and biocompatibility [9].

Herein, the porous carbon is facilely fabricated by thermal decomposition of copper-based metal-organic framework MOF-199 under inert atmosphere. The morphology, structure, and surface area of porous are investigated.

Experimental

Materials

$CuSO_4.5H_2O$ 99%, Benzene-1,3,5-tricarboxylic acid ($C_9H_6O_6$) 98%, NaOH 98%, HNO_3 65%, EtOH 99.7%,AR grade from China were used.

Preparation of MOF-199

Firstly, copper (II) hydroxide was prepared by mixing 60 mL $CuSO_4$ 0.1 M and 60 mL NaOH 0.2 M and stirred for 15 mins. The $Cu(OH)_2$ precipitate was filter, washed several times by deionized water.

Then, redispersed the $Cu(OH)_2$ into 200 mL deionized water. To that solution add slowly 200 mL benzene-1,3,5-tricarboxylic acid (H_3BTC) 0.02 M in ethanol. The mixture was stirred for an hour at room temperature. The product was filtered, washed several times by ethanol, and MOF-199 was finally obtained as a dark-blue powder by drying at 150°C for 12 hours.

Preparation of MOF-derived mesoporous carbon

MOF-199 material was carbonized at different temperatures (500, 600, 700°C) in inert atmosphere by blowing Ar through the heat chamber. The furnace was programmed to raise the heat at 5°C/min and held at designated temperature for 2 hours, and let to naturally cool to room condition to obtained a mixture of carbon and copper compound denoted as Cu/C. One part of the product was etched by HNO_3 10% solution to remove copper components.

Material characterizations

The chemical composition and morphology of the material was characterized by Energy-dispersive X-ray spectrometry (EDX) and by scanning electron microscope (SEM), respectively, both using Hitachi S-4600. The phase composition was determined by powder X-ray diffraction (PXRD) method on X'Pert Pro. XRD patterns were recorded using CuKα radiation (λ = 1.5406 Å). The porosity of materials was analyzed by nitrogen isotherm by Nova 2200E.

Results and discussion

The material phase was identified by PXRD method (Figure 1). Results from figure 1a showed that synthesized MOF-199 has cubic crystal structure with first four characteristic peaks at 6.7°, 9.33° , 11.6° , 13.3°, corresponding to (200), (220), (222), (400) faces. There is no other peak of copper salts and H_3BTC, indicating that the MOF is pure without any contaminants. The relatively low intensity peaks show that crystallinity of the material is relatively low due to the rapidly formation of product, even at room temperature:

$$CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4 \quad (1)$$

$$3Cu(OH)_2 + 2H_3BTC = Cu_3(BTC)_2 + 6H_2O \quad (2)$$

As the XRD patterns of materials under carbonization at 500, 600, 700°C were shown, the characteristic peaks of MOF-199 were disappeared, which indicate that the material was completely decomposed at experiment conditions. The carbon was in amorphous form as there is no relevant peak of the element. The formation of copper (at 43.6° and 50.8°) and cuprous oxide (36.5° and 42.1°) suggested the pyrolysis of MOF-199 was take place as following reactions:

$$Cu_3(C_9H_3O_6)_2 = 3CuO + 12C + 6CO + 3H_2O \quad (3)$$

$$2CuO + C = Cu_2O + CO \quad (4)$$

$$Cu_2O + C = 2Cu + CO \quad (5)$$

At 500 and 600°C, the Cu_2O peaks have higher intensity than that of Cu, meanwhile at 700°C, Cu is the dominant phase. This can be explained that in inert atmosphere, copper (II) oxide was reduced by C and CO to create lower oxidation state oxide. At higher temperature, the reduction takes place completely and metallic copper is primary phase.

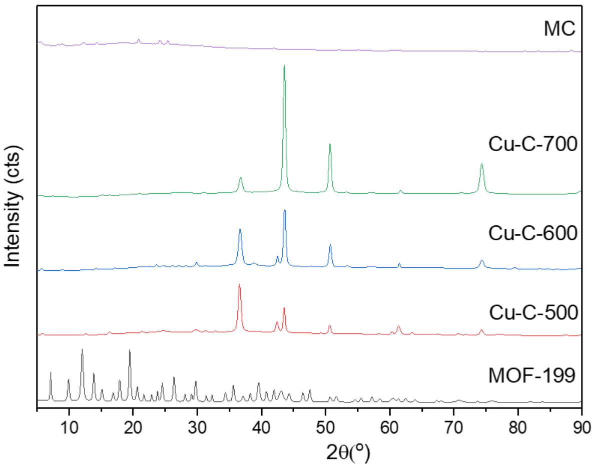

Figure 1: XRD patterns of MOF-199, Cu/C at different temperatures and mesoporous carbon

Treating Cu/C at 500°C with diluted HNO_3 solution yields the desired mesoporous carbon:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O \quad (6)$$

$$3Cu_2O + 14HNO_3 = 6Cu(NO_3)_2 + 2NO + 7H_2O \quad (7)$$

As shown, there is no crystalline phase in the final product, prove that the copper and copper oxide was thoroughly removed, leaving the amorphous mesoporous carbon.

The morphology of materials was studied by scanning electron microscope (Figure 2).

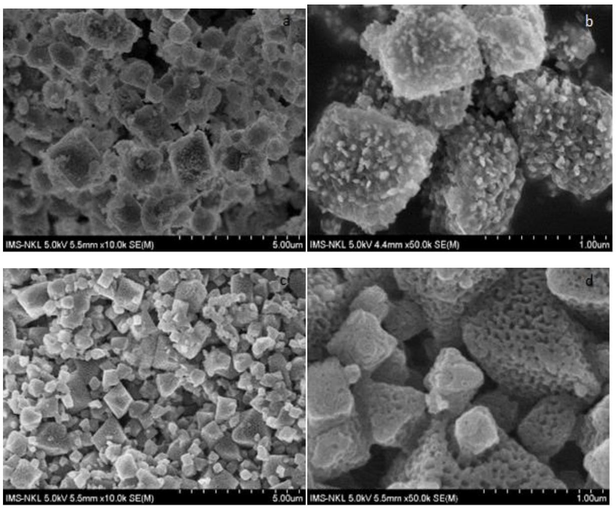

Figure 2: SEM images of a) MOF-199, b) Cu/C obtained by carbonization of MOF at 500°C, c) and d) mesoporous carbon

Figure 2a show the octahedral crystal shape that is characteristic to MOF-199 crystals, with particle size of about 1-2 μm, although the shape was not well-fined and the crystal is not homogeneous. The inhomogeneity was attributed to the fact that reaction between copper hydroxide (solid) and benzene-1,3,5-tricarboxylic acid (solute) is heterogeneous. Also the rapid reaction speed and the vigorous stirring prohibit the crystal to growth properly.

The microstructure of carbonized MOF at 500 °C is shown in Figure 2b. It can be seen that the material retains the octahedral morphology of MOF-199, with the same overall particle size of 1-2 μm. The carbon frame has small holes all over its surface, which be blocked by smaller particulates. These particulates have brighter image, indicate good electrical conductivity, which can be attributed to the metallic copper.

Figure 2c and d illustrate the morphology of mesoporous carbon at different magnifications. At high resolution of SEM image (figure 2c), the particles shape and size are identical to that of previous materials. Figure 2d provides the closer look at surface of the mesoporous carbon. It can be seen that the carbon framework is virtually impervious to the acid attack; on the contrary, metal copper and copper oxide are susceptible to corrosive in HNO_3 media and etched away by the acid, exposing the holes to porous canal inside the material, making the cavity accessible to adsorbates.

Table 1: Composition of mesoporous carbon obtained

Element	Weight (%)	Atomic (%)
C	76.24	81.04
O	23.76	18.96
Total	100	100

Material composition of the final porous carbon was measured by energy-dispersive X-ray spectroscopy (EDX). Percentage of each element was listed in table 1.

The absence of other element confirms the complete removal of copper component. Meanwhile, a high oxygen content shows that the mesoporous carbon was successfully activated by the acid.

The BET surface area of materials was determined by N_2 adsorption isotherm at 77K, results are shown in table 2.

Table 2: BET surface area of materials

Materials	BET surface area (m^2/g)
MOF-199	1083
Cu/C 500°C	201
Cu/C 600°C	98
Cu/C 700°C	17
Mesoporous carbon	375

It can be clearly seen that the porous framework of MOF-199 is of the specific surface area of 1083 m^2/g, which indicates that MOF materials was successfully synthesized via facile and quick route at ambient conditions. Even though, this surface area of MOF-199 is lower than theoretical value (about 1600 m^2/g), however, the synthesizing approach was simpler and scalable for mass production.

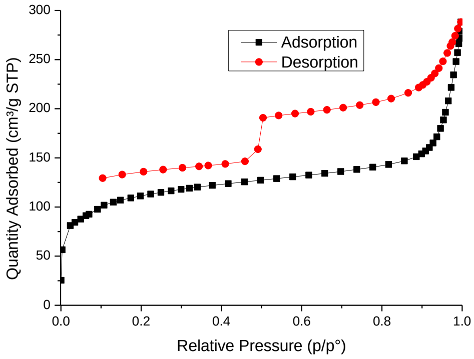

Figure 3: The N_2 adsorption-desorption isotherm of synthesized mesoporous carbon

After carbonization, the surface area of resultant Cu/C materials are decreased along with increase of carbonized temperature. Higher carbonized temperatures resulted in lower surface area of obtained Cu/C materials. It can be explained that at higher heat conditions, the original framework of MOF-199 was ease to collapse. The entire collapse of MOF framework is confirmed at carbonized temperature of 700°C with Cu/C surface area of only 17 m^2/g. Based on the experimental results, the sample at 500°C was chosen as the best carbonized temperature for making the mesoporous carbon.

The N_2 adsorption-desorption isotherm of the final product was shown in figure 3. Results show that the material has high surface area, at 375 m^2/g, nearly double the pre-treated sample, and average pore size of 4.7 nm. The broad hysteresis loop of N_2 adsorption-desorption indicates type IV isotherm. The removal of copper compound is not only eliminated the heavy, non-porous component, but also got rid of particulate that blocking the holes to the cavity of the spongy carbon framework. The steepness of desorption step reflects the pore blocking where larger pores are connected through smaller pore necks (bottle neck capillary). In the figure, the hysteresis loop is not closed, show the incomplete desorption of trapped N_2 molecules.

The pore size distribution of final product was shown in figure 4. It can be clearly seen that the material contain very homogenous pores, as pore volume contribution is mostly from pores which sizes in range of 4-4.2 nm.

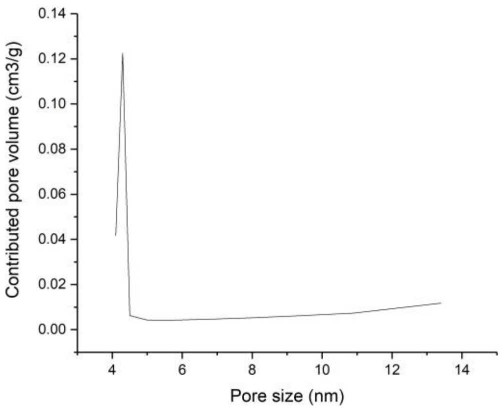

Figure 4: Pore size distribution of synthesized mesoporous carbon

Conclusion

MOF-199 was successfully synthesized by a quick and simple route at ambient conditions, as confirmed by PXRD method. The material has octahedral morphology and high surface area at more than 1000 m^2/g. Using MOF-199 as source of porous carbon framework, mesoporous carbon was prepared by carbonization of said MOF at 500°C for 2 hours, then wash the metal components by diluted HNO_3. The SEM images show that the octahedral morphology is preserved in the final product. The obtained mesoporous carbon has spongy structure with surface area of 375 m^2/g.

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