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# Influence of temperature on the carbonization context, oxidation properties and mechanism of a porous biomorphic carbon template

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A porous biomorphic carbon template (BCT) was prepared using a carbonized native aspen under an Ar atmosphere. Microstructural properties of the BCT were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). Non-isothermal oxidation properties and the mechanism of the BCT formation were studied by thermogravimetric analysis (TGA). Experimental results show that microstructure of the BCT exhibits a honeycomb interconnected porous network and double-peaked distribution of pore diameters. The BCT phase belongs to amorphous carbon, with an increase of the carbonization temperature, the (002) peak of the XRD spectrum becomes stronger, the interplanar spacing decrease, and the structure of BCT slowly evolved towards that of ideal graphite. The non-isothermal oxidation process of BCT is controlled by a chemical reaction and gas diffusion together, and the two stages have different influences on the whole reaction rate with an increase of the conversion (a). The corresponding activation energy  $(E_a)$  is also calculated.

Key words: biomorphic carbon template, structure properties, oxidation mechanism.

# Introduction

A biomorphic template is a new concept for fabricating ceramic materials with novel hierarchical and complex microstructures using natural biological materials as templates, such as wood [1], rattan [2], rice husk [3] etc.. Amongst these, wood has been paid considerable attention with respect to the conversion of its tissue to ceramic materials because it has highly anisotropic cellular structures [4]. Wood has been used to fabricate various novel ceramics with micro-, meso- and macro-structures, classified into the different groups according to the density or porosity of the products. Several research groups have developed bio-templating high temperature techniques to convert biological structures into ceramic materials [1, 5, 6].

Wood-derived cellular ceramics might be of interest for high-temperature-resistant exhaust gas filters, catalyst carriers, advanced microreactor systems, immobilization supports for living cells, microbes or enzymes, and waste water treatment, as well as acoustic and heat insulation structures, etc [7-9].

For the wood-derived cellular ceramics, the microstructure and thermal oxidation properties of the porous carbon template have an important influence on the structure and performance of the porous ceramics produced. However, little work has been done on a study of the microstructure and thermal oxidation properties of BCT systemically.

TGA methods (thermogravimetry, differential thermogravimetry) are widely used in the process of studying the thermal oxidation properties of carbon materials [10, 11]. The results of thermal analysis can supply very useful information on the oxidation mechanism of these types of materials and their thermal oxidation stability.

In the present study, a porous biomorphic carbon template (BCT) material was obtained from carbonizing aspen under an inert atmosphere. The structural properties of BCT were investigated by XRD, SEM and EDS techniques. Non-isothermal oxidation properties and the mechanism of BCT formation were investigated by thermogravimetric analysis (TGA) using a model-free kinetic method [12, 13].

# **Experimental**

## Material preparation

Native aspen was shaped, dried at 120 °C for 48 h, and subsequently carbonized at 900 °C, 1300 °C, 1500 °C and 1700 °C (aim temperature), respectively. Four types of porous biomorphic carbon templates (BCT) with different microstructures were obtained. The carbonization process was 2 K·minute<sup>-1</sup> between room temperature and 600 °C, 5 K·minute<sup>-1</sup> from 600 °C to the aim temperatures, then hold for 4 h at the aim temperatures. The carbonization condition was under Ar atmosphere with a flow-rate of 50 ml·minute<sup>-1</sup> in a graphite heated furnace [14].

## **Characterization of BCT**

The extent of carbonization was estimated from X-ray

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diffraction (XRD, D5000, Siemens) using an X-ray Diffractometer with a nickel filtered Cu  $K_a$  radiation produced at 30 kV and 30 mA. Scanning speeds were 2° minute<sup>-1</sup> to record all possible profiles and for calculations of XRD parameters, respectively. From the position of the (002) peak ( $2q_{(002)}$ ) in the X-ray diffractogram, the  $d_{(002)}$  interplanar spacing was determined using the Bragg equation:

$$d_{(002)} = \frac{\lambda}{2sin\theta_{(002)}} \tag{1}$$

Density and bulk porosity, which referred to the volume fraction of pores of a BCT, were calculated by the Archimedes method.

The morphology and quantitative elemental analyses of the BCT were characterized by a scanning electron microscope (SEM, JSM-6700F, Jeol) equipped with an energy dispersive X-ray spectrometry (EDS, Oxford) attachment.

The oxidation properties and mechanism of formation of BCT was characterized by thermogravimetry analysis (TGA, STA409C, Netzsch) in flowing air at 50 ml·minute<sup>-1</sup> with a heating rate of 5, 10 and 15 K·minute<sup>-1</sup> from room temperature to 700 °C, with alumina powder as the reference sample. The Netzsch thermal analysis software was used for evaluating the data. This software permits one to evaluate weight changes of a sample (thermogravimetric curve) and the single differential thermal analysis curve (obtained in the absence of a reference sample by difference of the sample temperature and the reference temperature calculated with the application of a mathematical model).

#### Theoretical background of model-free kinetic analysis

Model-free kinetics is based on an iso-conversional computational technique that calculates the effective activation energy ( $E_a$ ) as a function of the conversion (a) of a chemical reaction, E = f(a). The conversion (a), temperature (T) and time (t) are the three factors influencing the reaction rate of a chemical reaction. The reaction rate represented as function of conversion f(a) is different for each process and must be determined experimentally. The model-free kinetics is a computer program option basing on the theory of Vyazovkin and Flynn-Wall-Ozaw.

In their approach, no model is applied. The data in this approach is gathered during numerous experiments. The approach follows all points of conversion from multiple experiments instead of a single one [12]. The theory is based on the assumption that:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{2}$$

where f(a) represents a reaction model and k(T) the Arrhenius rate constant. The activation energy  $E_a$  is constant for a certain value of conversion a (this is called the iso-conversional method). Taking the reaction rate equation,

presented as f(a) and dividing by the heating rate  $\beta = dT/dt$ , one obtains:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \Rightarrow \frac{d\alpha}{dT} = \frac{k}{\beta}f(\alpha)$$
(3)

where da/dt is the reaction rate (s<sup>-1</sup>), k the velocity constant (s<sup>-1</sup>), a the conversion, and b the heating rate (K·s<sup>-1</sup>). Substituting k by the Arrhenius expression  $k = k_0 \cdot e^{-E/RT}$  and rearranging gives:

$$\frac{1}{f(\alpha)}d\alpha = \frac{k_o}{\beta}e^{-E/RT}dT$$
(4)

Integrating up to conversion, a (at a temperature T) gives:

$${}^{\alpha}_{0}\frac{1}{f(\alpha)}d\alpha = g(\alpha) = \frac{k_o}{\beta}\int_{T_0}^{T} e^{-E/RT}dT$$
(5)

Since E/2RT >> 1, the temperature integral can be approximated by:

$$\int_{T_0}^{T} e^{-E/RT} dT \approx -\frac{R}{E} \cdot T^2 \cdot e^{-E/RT}$$
(6)

Substituting the temperature integral, rearranging and logarithming, one obtains the Vyazovkin equation:

$$ln\frac{\beta}{T_{\alpha}^{2}} = ln\left[\frac{Rk_{o}}{E_{a}g(\alpha)}\right] - \frac{E_{\alpha}}{R}\frac{1}{T_{\alpha}}$$
(7)

The equation (5) can be reaarranged as:

$$g(\alpha) = \frac{k_o}{\beta} \int_{T_0}^T e^{-E/RT} dT = \frac{k_o E}{\beta R} \int_{\infty}^u \frac{-e^{-u}}{u^2} du = \frac{k_0 E}{\beta R} \cdot P(u)$$
(8)

where

$$u = \frac{E}{RT} \qquad dT = \frac{E}{Ru^2} du \qquad (9)$$

According to Doyle approximation [13], one obtains:

$$LogP(u) = -2.315 - 0.4567 \frac{E_a}{R} \frac{1}{T_a}$$
(9)

Combines the equation (7) and (8), one obtains Flynn-Wall-Ozaw equation:

$$Log\beta = Log\left[\frac{K_{0}E_{a}}{Rg(a)}\right] - 2.315 - 0.4567\frac{E_{a}}{R}\frac{1}{T_{a}}$$
(10)

The two (equation (7) and (10)) are defined as dynamic equations, which are used for the determination of the activation energy for all conversion values (a).

# **Results and Discussion**

#### Microstructure characterization of BCT

Fig. 1 shows SEM micrographs of BCT (carbonized at 1300 °C). As seen in Fig.1(a) and (b), it is easy to see that a microstructure similar to a blood vessel existed in



Fig. 1. SEM micrographs of (a, b) cross sections perpendicular to the axial direction and (c) cross section parallel to the axial direction of a biomorphic carbon template (BCT).

the template. When carbonized under an Ar atmosphere, the organic cell wall of aspen wood turned into carbon wall and the cell cavities turned into pores. The pores can be classified into two groups, namely there is doublepeaked diameter distribution, depending on their average diameters: small pores (noted by "A"), and large pores (noted by "B"), these form honeycomb structures. The average diameters of each group are about 15-30 mm for the large pores, 4-10 mm for the small pores. Most of the pores show different shapes, such as ellipses, triangles, circles, etc.. From Fig.1-c, the hollow channels of various diameters that originate from tracheid cells are parallel to the axis of the aspen.

Table. 1 displays the component EDS data of BCT (carbonization at 1300 °C) measured with the same SEM system. It can be seen clearly that the main element of BCT is carbon, the ratio of C : O : K : Mg : Ca : S are 93.21 : 4.45 : 0.64 : 1.02 : 0.38 : 0.30 in atom amounts. The origins of K, Ca, Mg and S elements are the inorganic salt absorbed in aspen growth process.

Table 1. The component EDS data of BCT

Element	С	0	Κ	Ca	Mg	S	Total
Weight/%	88.40	5.55	2.09	3.34	0.74	0.24	100.00
Atom/%	93.21	4.45	0.64	1.02	0.38	0.30	100.00

## **XRD** analysis of BCT

Fig. 2 shows the XRD spectra of BCT obtained from the carbonization at different temperatures. Two broad diffraction peaks are observed, indicating that the BCT is amorphous. For BCT carbonization at 900 °C, it can be seen that there are two main analogous graphitic peaks corresponding to a broad (002) peak and a lower intensity (10*l*) peak, which is suggestive of the development of hexagonal network layers stacked roughly parallel to each other, i.e. the micro-scale of this material is a turbostratic



Fig. 2. XRD patterns of BCT treated at different temperature.

structure [15], which also indicates the regularity of carbon in BCT is poor.

Judging from the intensity and shape, the peak (002) profile of the carbon template consists of three components that correspond to amorphous (B), turbostratic (T) and graphitic (G) components [16]. From Fig. 2, it can also be seen that the (002) peak becomes stronger, shifts to larger 2q, and has a smaller full-width at half-maximum intensity with an increase in the carbonization temperature from 900 to 1700 °C, as expected for carbonized cellulose [15], which means that the T and G components increase and the B component decreases. This implies that the regularity of the carbon atoms in the carbon template became better; consequently their structure became more rigid and stable.

The narrowing of the (002) peak is indicative of a developing atomic order in the BCT. It is noted that the profile of the (10*l*) peak changes from a symmetric one below 1500 °C to asymmetrical for 1700 °C, revealing the turbostratic structure of BCT. However, it seems that three-dimensional crystallinity is almost not developed even after carbonization at 1700 °C because the (004) peak and the splitting of the (10*l*) peak to (100) and (101) peaks can hardly be observed.

The  $d_{(002)}$  value is traditionally used to estimate the degree of graphitization of carbon. In general, growing disorder in the material is reflected in increased values of  $d_{(002)}$  [17]. As shown in Fig. 2, the (002) inter-planar spacing of the crystalline decreases with an increase of the carbonization temperature, which means the structure of BCT slowly evolved towards that of ideal graphite. Crystalline graphite exhibits a sharp peak and an interplanar spacing close to 0.3354 nm [18]. All  $d_{(002)}$  values of BCT are much higher than that of ideal graphite, indicating the non-graphitizable characteristics of BCT. These results also suggest that BCT carbonized at experimental temperatures is not composed of a completely graphitized carbon, but has a turbostratic structure [19, 20].

Fig. 3 shows the bulk porosity and density of BCTs carbonized at different temperatures. It can be clearly seen that the bulk porosity increased and density decreased



**Fig. 3.** The bulk porosity and density of BCT treated at different temperatures.

with an increase of the temperature.

#### Non-isothermal oxidation properties of BCT

Fig. 4 shows the TG-DTG curves of BCT (carbonized at 1300 °C) with different heating rates under an air atmosphere. From the TG curves, it can be clearly seen that the oxidation weight-loss of BCT increases with an increase of the temperature, and the initial and final temperature of the oxidation reaction increase when the heating rate increases.

From the DTG curves, irrespective of the heating rate, it is easy to see that the oxidation rate (da/dT) of BCT increases initially and then decreases with an increase of the temperature.

Combined the data from the TG and DTG curves, it can be seen that the oxidation rate increases initially and then decreases with an increase of the weight-loss , it is up to maximum when the weight-loss is 38.6% for 10 K·minute<sup>-1</sup>. Thus, the characteristic of this reaction is a self-accelerating process from 421.5 to 465.4 °C for 10 K·minute<sup>-1</sup>.

As shown in Fig. 2 (XRD pattern), the BCT has a turbostratic microstructure, which has a few unsaturated carbon atoms (which could react with oxygen, Abbr as: ACA) on the material surface [21]. Thus, it has the



Fig. 4. TG-DTG curves of BCT with different heating rates.



lowest oxidation rate at the initial oxidation stage.

As the oxidation reaction proceeds, the chemical bonds composed of the turbostratic microstructure on the microscale (C-C, C = C, etc.) of the material should be broken off by the oxidation to form more unsaturated carbon atoms, thereby increasing the ACA. Thus, with an increase of the weight loss, the amount of ACA increases, the reaction rate also increases. So a self-accelerating characteristic is displayed.

When the weight loss is bigger than a critical value (the value is 61.4% for 10 K·minute<sup>-1</sup>), the amount of ACA decreases with an increase of the weight loss, and the oxidation rate decreases.

#### Model-free method kinetic analysis

In the present study, three heating curves of BCT materials oxidation reaction were used, obtained in the temperature range of 300-550 °C with heating rates of 5,10 and 15 K·minute<sup>-1</sup> as shown in Fig. 4. The whole oxidation process of BCT was chosen for model-free kinetic calculations.

In accordance with model-free kinetics, for each conversion a,  $lnb/T_a^2$  was plotted versus  $1/T_a$  for the Vyazovkin method and lnb was plotted versus  $1/T_a$  for the F-W-O method, giving straight lines with a slope  $E_a/R$ ; Therefore the activation energy was obtained as a function of conversion.

Fig. 5 presents the  $E_a$  of BCT oxidation reaction as a function of *a* (the oxidation weight loss data of BCT were obtained from Fig. 4). It can be clearly seen that the  $E_a$  value slightly increases, and then decreases slowly with an increase of a. Both curves obtained from K-A-S and F-W-O methods have the same tendency. The  $E_a$  value is up to maximum (166.1 kJ·mol<sup>-1</sup> for K-A-S method) when the *a* equals to 32.5% and the minimum value (78.4 kJ·mol<sup>-1</sup> for K-A-S method) lies at the end of the dependence.

Vyazovkin and others [22-24] have studied the phenomena clearly, and proposed the concept of a variable activation energy as a compromise between the actual complexity of solid state reactions and oversimplified methods of describing their kinetics. They call the variable  $E_a$  as an



Fig. 5.  $E_a$  as a function of a for BCT oxidation determined using the model-free methods.

"effective  $E_a$ " and think that the process with a variable activation energy not only involves chemical reactions, but also contains physical processes, for instance, sublimation, adsorption, desorption, diffusion of gaseous product, etc. The variation of activation energy with the extent of conversion is attributed to the relative contribution of each single-step process. Therefore, the effective activation energy of a solid state reaction is generally a composite value determined by the activation energies of various processes and by their influence on the overall reaction rate.

According to Ref [25] and combined with the above discussion, it is known that the oxidation process of BCT mainly contains two elementary steps of a chemical reaction and gas diffusion, Therefore, the effective  $E_a$  of BCT the oxidation process is a composite value (Fig. 5) determined by the  $E_a$  of the two single-step processes and by their influence on the overall oxidation rate [26].

According to the dependence of  $E_{\alpha}$  on  $\alpha$  obtained by the model-free methods, the oxidation mechanisms of BCT are obtained.

In the first stage of BCT material oxidation reaction  $(a \le 32.5\%, T \le 441.0 \text{ °C} \text{ for } 10 \text{ K·minute}^{-1})$ , a plateau trend indicative of a single-step process is observed. In this stage, the temperature is low and the amount of ACA on the reaction interface of BCT is small, so the chemical reaction rate is small. The oxygen diffusing into the interior reaction interface through hollow channels is big enough for the oxidation reaction. In this condition, gas diffusion makes little influence to the whole reaction rate. So the oxidation process is controlled by chemical reaction and the corresponding  $E_a$  is 162-166 kJ·mol<sup>-1</sup>.

In the second oxidation stage (a > 32.5%, T > 441.0 °C for 10 K·minute<sup>-1</sup>), the variation of  $E_a$  indicates that this stage is controlled by the chemical reaction and gaseous diffusion together. In this stage, due to the non-isothermal heating process, the chemical reaction rate increases rapidly with an increase of the temperature and a, the reaction interface needs more and more oxygen, the reaction product (CO or CO<sub>2</sub>), exists in the reaction interface and also needs to diffuse out at the same time. For the amount and interfacial area of hollow channels and the temperature increase as the oxidation proceeds, the gas diffusion rate becomes rapid.

As we know, the chemical rate varies exponentially with T and diffusion is a much weaker function, thus with an increase of the temperature, the increase of the reaction rate exceeds that of gas diffusion slowly. In this condition, the gas diffusion has more and more influence on the whole reaction with the an increase of the temperature and a. Because the  $E_a$  of gas diffusion is smaller than that of the chemical reaction, the effective  $E_a$  decreases with an increase of a (Fig. 5). The minimum value of  $E_a$  (68.9-78.4 kJ·mol<sup>-1</sup>) lies at the end of the dependence.

#### Conclusions

In the present study, porous biomorphic carbon templates

(BCT), which retain the anatomical features of aspen, were prepared by carbonizing native aspen under an Ar atmosphere through a controlled heating process. The microstructural characterization and oxidation mechanisms of BCT were investigated. The results are summarized as follows:

(1) The phase of BCT materials obtained is amorphous. With an increase of the carbonization temperature, the (002) peak of the XRD spectrum becomes stronger, the interplanar spacing decrease, the structure of BCT slowly evolved towards that of ideal graphite, also the density increase and bulk porosity decrease.

(2) The BCT shows a honeycomb interconnected porous network and a double-peaked diameter distribution of pore.

(3) The non-isothermal oxidation properties of BCT exhibit a partial self-accelerating characteristic.

(4) The model-free method kinetic analysis results show that the  $E_{\alpha}$  depends strongly on  $\alpha$ . The oxidation reaction of BCT is a complex process: when  $\alpha \le 32.5\%$ , oxidation is mainly controlled by a chemical reaction, and the corresponding  $E_a$  value is about 160 kJ·mol-<sup>1</sup>; when a > 32.5%, the oxidation is controlled by a chemical reaction and gas diffusion together, and the gas diffusion has more and more influence on the whole reaction rate, which led to a decrease of  $E_a$ .

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Pengzhao Gao, Pengfei Hu, Wenxiang Wang and Weiwei Gong

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