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# Model-free kinetics applied to an oxidation mechanism of a biomorphic carbon template derived from pine

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A biomorphic carbon template (BCT) was developed by carbonizing pine under vacuum. Structural and oxidation properties of BCT were evaluated by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and thermogravimetric analysis (TGA). Experimental results show that BCT has a topologically uniform interconnected porous network microstructure, and is typical non-graphitizable carbon containing C = C bonds, C–O–C bonds and a C–H structure. The non-isothermal oxidation properties of BCT exhibit a partially self-accelerating characteristic; the oxidation process of BCT is firstly controlled by a chemical reaction, and then controlled by a chemical reaction and gas diffusion together, which is obtained from a Vyazovkin model-free method, and the corresponding activation energy ( $E_a$ ) is also calculated.

Key words: biomorphic carbon template, Vyazovkin model-free method, self-accelerating.

## Introduction

The design of novel ceramic materials with specific functional properties and structures by mimicking the hierarchical cellular structure of wood has recently attracted particular interest [1-3]. Wood is a naturally grown composite material of a complex hierarchical cellular structure, and comprised of elongated tubular cells aligned with the axis of the tree trunk and growth ring structures. The tubular cells of wood with a preferential orientation in the axial direction offer the possibility to use various infiltration techniques to transform the bio-organic wood structure into an inorganic ceramic material with tailored physical and mechanical properties, several research groups have developed bio-templating high temperature techniques to convert biological structures into ceramic materials [2, 4, 5].

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. 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 the 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 solid materials [6, 7]. The results of thermal analysis can supply very useful information on the processes of oxidation decomposition of these types of materials and their thermal oxidation stability.

In the present study, the biomorphic carbon template (BCT) was made by carbonizing pine under vacuum. The structural characterization of the BCT was investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform-infrared (FT-IR) spectroscopy techniques. Non-isothermal oxidation properties and the mechanism of BCT were investigated by thermogravimetric analysis (TGA) using a Vyazovkin model-free kinetic method [8].

## **Experimental**

#### Material preparation

Pine wood was shaped, dried at 120 °C for 48 h, and subsequently carbonized under vacuum at 1200 °C for 4 h in a graphite heater furnace with a slow heating rate of 2 K·minuter<sup>-1</sup>up to 600 °C and a higher rate of 5 K·minuter<sup>-1</sup> up to the peak temperature, resulting in a biomorphic porous carbon (BCT), whose porosity was 45.1%, density was  $0.276 \text{ g}\cdot\text{cm}^{-3}$ , and specific area was about 500-600 m<sup>2</sup>·g<sup>-1</sup>.

## Structure characterization of BCT

The microstructural morphology of BCT was observed with a scanning electron microscope (SEM, JSM-6700F JEOL) operated at 20 kV and 20 mA.

The XRD pattern of BCT was recorded using an X-ray diffractometer (XRD D5000, Siemens) with nickel filtered Cu  $K_{\alpha}$  radiation produced at 35 kV and 20 mA.

Fourier transform infrared spectroscopy (FTIR) studies were performed with a Fourier transform infrared spect-

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rometer (AVATAR 360 FT-IR, Nicolet) in the wavenumber range of 4000-500 cm<sup>-1</sup>. The spectra of samples were recorded by transmission in a dry air atmosphere through a pastille made of a few milligrams of sample materials mixed with KBr.

#### **Oxidation properties tests of BCT**

The oxidation properties and mechanism of BCT were measured using thermogravimetric analysis (TGA) in flowing air with a heating rate of 5, 10, 15 and 20 K·minuter<sup>-1</sup> from room temperature to 700 °C.

TGA was performed on a TGA-DSC thermal analyzer (STA 449C, Netzsch Thermische Analyser) with alumina powder as the reference sample. Netzsch thermal analysis software was used to evaluate the data. This software permits one to evaluate weight changes of a sample (thermogravimetric curve) and a 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**

The reaction rate of a chemical reaction depends on the conversion ( $\alpha$ ), temperature (*T*) and time (*t*). The reaction rate represented as a function of the conversion  $f(\alpha)$  is different for each process and must be determined experimentally.

For simple reactions, the evaluation of  $f(\alpha)$  with an nth order is possible. For complex reactions the functions of  $f(\alpha)$  are complicated and generally unknown; in this case, the nth order algorithm causes unreasonable kinetics data. With the model-free kinetics more accurate evaluations of complex reactions can be performed, as a trustworthy way of obtaining reliable and consistent kinetic information about the overall process [9].

Vyazovkin [8] developed an integral kinetic method where no model has to be selected (model-free kinetics), which allows the evaluation of both simple and complex reactions, using multiple heating rates.

The theory is based on the assumption that:

$$\frac{da}{dt} = k(T)f(a) \tag{1}$$

where  $f(\alpha)$  represents the reaction model and k(T) the Arrhenius rate constant and that the activation energy  $E(\alpha)$  is constant for a certain value of conversion *a* (iso-conversional method). Taking the reaction rate equation, presented as  $f(\alpha)$  and dividing by the heating rate  $\beta = dT/dt$ , one obtains:

$$\frac{da}{dt} = k(T)f(a) \Longrightarrow \frac{da}{dT} = \frac{k}{\beta}f(a)$$
(2)

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

$$\frac{1}{f(a)}da = \frac{k_o}{\beta}e^{-E/RT}dT$$
(3)

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

$$\int_{0}^{a} \frac{1}{f(a)} da = g(a) = \frac{k_o}{\beta} \int_{\Gamma_0}^{T} e^{-E/RT} dT$$
(4)

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

$$\int_{a}^{T} e^{-E/RT} dT \approx \frac{R}{E} \cdot T^2 \cdot e^{-E/RT}$$
(5)

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

$$ln\frac{\beta}{T_a^2} = ln\left[\frac{Rk_o}{E_ag(a)}\right] - \frac{E_a}{R}\frac{1}{T_a}$$
(6)

This is defined as a dynamic equation, which is used for the determination of the activation energy for all conversion values ( $\alpha$ ).

## **Results and Discussion**

#### **Microstructure characterization**

Fig. 1 shows the SEM micrographs of the BCT. As seen in Fig. 1, the microstructure of the BCT shows hollow channels of various diameters that originate from tracheid cells which are parallel to the axis of the tree (as shown in Fig.1(b), (c)). Hollow channels of the biocarbon template have a uniform arrangement, where the black part is lumen and grey part is carbon layer formed by carbonization of the cell wall (as shown in Fig.1(a), (b)). The difference of diameters of hollow channels is attributed to the non-uniform distribution of the texture in the wood. The average diameter of cells is about 5-30 µm, and the cell wall (thickness of carbon layer) is about 2-3 µm. Most of the cellular pores show a rectangular shape and the whole shows a regular net distribution with carbon layers join each other. The cell topologically uniform arrangement of early wood is interrupted by growth ring patterns, where late wood cells show a significantly higher strut thickness.

## **XRD** analysis

Fig. 2 shows the XRD pattern of the BCT. It can be seen from Fig. 2 that there are two main analogous graphitic peaks corresponding to a broad (002) peak and a lower intensity (10*I*) peak. This strongly reveals that BCT is in a partly graphitized amorphous state, and has a turbostratic microstructure [10]. There is not a broad peak at  $2\theta \approx 18.5^\circ$ , which would be due to adjacent chains of a linear polymer [11].

#### **FT-IR** analysis

Fig. 3 shows the FT-IR spectrum of the BCT. In the FT-IR spectrum of the BCT, the broad peak at  $3418 \text{ cm}^1$  is the absorption peak of water. The peaks at  $2964 \text{ cm}^1$  and  $2880 \text{ cm}^1$  are attributed to aromatic and aliphatic C–H

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



Fig. 2. XRD pattern of the BCT.



Fig. 3. FT-IR spectra of BCT.

asymmetrical and symmetrical stretching vibrations, respectively. The peak at 1616 cm<sup>1</sup> may be assigned to aromatic C = C in-plane stretching vibrations. The peak at 1054 cm<sup>1</sup> is characteristic for C–O–C bonds. A distinct behavior of individual C = O bands (at 1710 and 1740 cm<sup>1</sup>) for wood does not appear in the spectra of BCT. The peak at 717 cm<sup>1</sup> is ascribed to aromatic C–H and C–C out-of-plane vibrations [12], suggesting the formation of a mass polynuclear hydrocarbon structure [13]. These results show that BCT is a carbon based material containing C–O–C bonds, C = C bonds and a C–H structure, etc.

## Non-isothermal oxidation properties of BCT

Fig. 4 shows the TG-DTG curves of BCT with different heating rates. From the TG curves, it can be clearly seen that the oxidation weight-loss of the BCT began at about 400 °C, and increased with an increase of temperature. Also the initial and final temperatures of the oxidation reaction increase when the heating rate increased. 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.

Combining the results of the TG and DTG curves, it can be clearly seen that the oxidation rate increases initially and then decreases with an increase of the weight-loss, it is up to a maximum when the weight-loss is 54.37% for  $10 \text{ K}\cdot\text{minuter}^{-1}$ . Thus, the characteristic of this reaction is a self-accelerating process from 400 to 528.1 °C for  $10 \text{ K}\cdot\text{minuter}^{-1}$ .

As shown in Fig. 2 (the XRD pattern), the BCT has a turbostratic microstructure and has a few unsaturated carbon atoms (which could react with oxygen, Abbr as: **ACA**) on the BCT material surface [14]. Thus, the material has the lowest oxidation rate in the initial oxidation stage.

As the oxidation reaction proceeds, the chemical bonds (C-C, C-O-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, and the reaction



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

rate also increases. So a self-accelerating characteristic is displayed.

When the weight loss is bigger than a critical value (the value is 54.37% for 10 K·minuter<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

Model-free kinetics requires at least three dynamic curves with different heating rates. In the present study, there are four heating curves of the BCT oxidation obtained in the temperature range of RT-700 °C with heating rates of 5, 10, 15, and 20 K·minuter<sup>-1</sup>shown in Fig. 4.

In accordance with Vyazovkin model-free kinetics, for each conversion  $\alpha$ ,  $\ln\beta/T_{\alpha}^2$  was plotted versus  $1/T_{\alpha}$ , giving a straight line with the slope  $-E_{\alpha}/R$ ; therefore the  $E_{\alpha}$ was obtained as a function of conversion.

Fig. 5 presents the  $E_a$  of the BCT oxidation reaction as a function of  $\alpha$ . It can be clearly seen that the  $E_a$  value slightly increases, and then decreases with an increase of the percentage conversion. The  $E_a$  value is up to maximum (129.7 kJ·mol<sup>-1</sup>) when  $\alpha$  equals to 30% and the minimum value (74.5 kJ·mol<sup>-1</sup>) lies at the end of the dependence.



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



Vyazovkin and other [15-18] 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 the "effective  $E_a$ " and think that a process with a variable activation energy not only involves chemical reactions, but also contains physical processes, for instance, sublimation, adsorption, desorption, diffusion of gaseous products, etc. The variation of the 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 [19] and combined with the above mentioned, it is known that oxidation process of the BCT mainly contains two elementary steps of a chemical reaction and gas diffusion, Therefore, the effective  $E_a$  of the BCT 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, [20]:

$$\beta \frac{da}{dT} = f_c(\alpha) k_c(T) + f_d(\alpha) k_d(T)$$
(7)

where the subscripts c and d stand for the chemical reaction and gas diffusion, respectively.

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

In the first stage of the BCT oxidation reaction ( $a \le 30\%$ ), a plateau trend indicative of a single-step process is observed. In this stage, the amount of ACA on the reaction interface is small and the chemical reaction rate is slow. The oxygen diffusing into the interior reaction interface of the BCT through hollow channels is enough for the oxidation reaction, and the concentration of oxygen is almost the same over all the hollow channels. In this condition, gas diffusion was little influence on the whole reaction rate ( $f_d(a)k_d(T)$ equaled to zero approximatively). So the oxidation process is initially controlled by the chemical reaction. The corres512

ponding  $E_a$  is 120-130 kJ·mol<sup>-1</sup>.

In the second oxidation stage (a > 30%), the variation of  $E_a$  indicates that this stage is controlled by the chemical reaction and gaseous diffusion together. In this stage, due to a non-isothermal heating process, the chemical reaction rate increases rapidly with the increase of conversion, and hollow channels of the BCT are filled with reactant (O<sub>2</sub>) and product (CO and CO<sub>2</sub>). For the ACA inside the BCT, the oxygen must diffuse through the gas layer to react with carbon, simultaneously; the reaction product makes an inverse diffusion. The faster the chemical reaction rate, the harder the gas diffusion. Namely, with an increase of the conversion, the gas diffusion has more and more influence on the whole reaction rate (the  $f_d(\alpha)k_d(T)$  increases).

In this condition, the oxidation process of the BCT is controlled by the chemical reaction and gas diffusion together, and the gas diffusion was more and more influence on the whole reaction rate (the  $f_d(\alpha)k_d(T)$  increases) with the increase of  $\alpha$ . Because the  $E_a$  of gas diffusion is smaller (15 kJ·mol<sup>-1</sup> [14]) than that of the chemical reaction, the effective  $E_a$ decreases with an increase of  $\alpha$ (Fig. 5). The minimum value of  $E_a$  (74.5 kJ/mol) lies at the end of the dependence.

## Conclusions

In the present study, a biomorphic carbon template made from pine was developed. The basic structural characterization and oxidation mechanism of the BCT were investigated. The results are summarized as follows:

(1) The microstructure of BCT has a topologically uniform interconnected porous network microstructure, and is typical non-graphitizable carbon containing C = C bonds, C–O–C bonds and a C–H structure.

(2) The non-isothermal oxidation properties of the BCT exhibit a partially self-accelerating characteristic.

(3) 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  $\alpha \leq 30\%$ , oxidation is mainly controlled by the chemical reaction, and the corresponding  $E_a$  value is about 120-130 kJ·mol<sup>-1</sup>; when a > 30%, the oxidation is controlled by the chemical reaction and gas diffusion together, and the gas diffusion was more and more influence on the whole reaction rate, which leads to a decrease of  $E_a$ .

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