Study on Mechanism of Microwave Aided Co-Carbonization of Coal with Waste PET Plastic

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Abstract: The co-carbonized materials of coal and PET were prepared by microwave heating. The mechanism of co-carbonization is presented by thermogravimetric analysis and pyrolysis chromatography, combining with chemical changes of coal pyrolysis at lower temperature. The results show that the cracking reaction is dominated in synergistic carbonization prophase, while polycondensation in the late. Carbonization cracking of PET can promote carbonization of coal and formation of pore structure. The infrared adsorption peaks of –OH, O-H, -COOH and N-H disappear, the vibration intensity of N-H descends and the adsorption peaks of aromatic enhance, which prove the reactions of side chains break, decarboxylation reaction and oxygen-containing functional groups remove have taken place. The XRD analysis of co-carbonized materials shows that the materials take on disordered state in whole and microcrystalline graphite exists in part. The d (002) is large which results in the increase of the value of methylene blue and iodine sorption. It can provide theoretical foundation of the directional preparation of cheap and high performance activated carbon materials.

Keywords: Coal-based Activated Carbon, PET, Co-carbonization, Microwave Heating, Synergistic Effect

1 Introduction

In recent years, the problems of environmental pollution brought by plastic products are becoming more and more severe. According to statistics, the amount of waste plastics in China broke through 2010 Million tons but the recovery percent is less than 30%. How to solve the serious problems of “white pollution” is the one of great subject in contemporary [1-4].

On the theoretical basis of the co-coking of coal/waste plastic to prepare the carbon materials, on the one hand, it could make full use of the structural characteristics of coal and, on the other hand, it could make use the synergistic effect of coal/waste plastics to improve the coking property of coal and the performance of co-carbonization materials. Using coal and PET as raw materials and microwave aided has prepared the high performance active carbon and application for patent at present, this indicated that it is feasible to produce the high performance active carbon using the great synergistic effect of coal/PET, but now there is no report for the mature and practicable co-carbonization mechanism.

2 Experimental

2.1 Raw materials pretreatment and analysis

The coal sample of Shenfu was grinded using the vibration ball-milled system, and the particle size measured by laser Sizer was d50 ≤10 μm.

PET raw materials: Several abandoned colorless PET beverage bottles were eliminated covers, tips and bottoms of non-PET component. And then they were sheared into very small pieces, washed clean and dried. Caustic soda as chemical coating elimination agent was used to do surface cleaning, in order to remove of the pollutants adhering to surface of PET bottles. Subsequently, the materials were cleaned, dried and comminuted, as well as screening the particle with the size of less than 180 meshes.

The comminuted coal samples were dried in a vacuum drying oven at 105℃ for 4h to remove the water. About 2.5g cleaned samples were taken out to determine the its content of C, H, N and S on the elemental analyzer (Elementar, Vario EL III), with the instrumental standard deviation CHN<0.1% abs. The results of proximate and ultimate analyses were shown in Table 1 and Table 2.
2.2 Preparation of material of microwave-assisted co-carbonization of coal/PET

Experimental group I: 1.00g Shenfu coal, Experimental group II: 0.40g PET, Experimental group III: mix Shenfu coal (1.00g) with PET in a 1:0.4 proportion, Experimental group IV: mix Shenfu coal (1.00g) with KOH in a 1:3 proportion, Experimental group V: mix 0.40g Shenfu coal with 3.00g KOH, Experimental group VI: Mix Shenfu coal (1.00g), PET and KOH in a 1:0.4.3 proportions.

Cover up the coal in the pot into ceramic container with insulation material. And then the ceramic container was put into microwave oven (Glanz, Model NO. G80F23CN2L-A9, microwave frequency 2450MHz) and carbonized for 6.5min at the 450W power setting.

After cooling the products was treated by grind, acid cleaning (dilute hydrochloric acid, diluted the concentrated hydrochloric acid with water in 1.9 ratio), distilled water cleaning and drying, and then the products will be analyzed ulteriorly. The carbonization products of all experimental group are marked successively as AC I, AC II, ACIII, AC IV, AC V and AC VI. The methylene blue adsorption value is an essential parameter of characterization of adsorption of active carbon adsorbing material which can be measured expediently. This paper measured the methylene blue adsorption value in GB/T 7702.7-2008.

2.3 Carbonization process and product analytical methods

The thermal stabilities of samples were carried out using a thermogravimetric analyzer (TA, SDT Q600). The samples were heated from 35 to 85°C at a rate of 20°C min⁻¹ under the protection of nitrogen flow 100cm³/min.

Chromatography: Thermal desorption (TP-2020)/GC900A.

Fourier transform infrared (FTIR) spectra of the samples were obtained by using a spectrophotometer (PE, Spectrum GX, wave-numbers 400–4000 cm⁻¹) at a scanning number of 32 with the KBr sampling method.

X-ray diffraction analysis was conducted on an X-ray diffractometer (Rigaku, D/MAX-2400) with Cu-Ka radiation (λ = 1.5406 nm),) at a voltage and current of 46 kV and 100 mA.

3 Results and Discussion

3.1 Preparation and methylene blue adsorption of charring materials

The results of methylene blue adsorption experiments for all carbonization products as followed:

<table>
<thead>
<tr>
<th></th>
<th>mg·g⁻¹</th>
<th>g·m⁻³</th>
<th>mg·g⁻¹</th>
<th>g·m⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.59</td>
<td>1.87</td>
<td>0.45</td>
<td>1.87</td>
</tr>
<tr>
<td>II</td>
<td>0.74</td>
<td>1.87</td>
<td>0.207</td>
<td>1.87</td>
</tr>
<tr>
<td>III</td>
<td>0.344</td>
<td>1.87</td>
<td>0.344</td>
<td>1.87</td>
</tr>
</tbody>
</table>

The adsorption capacity of methylene blue of AC IV and AC VI is greatly higher than that others', this illustrated that shenfu coal could be made into active carbon with the higher activities by potassium hydroxide. Further analyses, the adsorption capacity of methylene blue of AC VI is higher than that AC IV, this shows that shenfu coal and PET exists the great co-carbonization synergistic effect.

3.2 Mechanism analysis of co-carbonization of shenfu coal and PET

The TG curve of experimental group VI are showed in Figure 1, that have the number of significant regional rapid weight loss between 50°C~300°C, in which the weight loss of around 100°C was mainly adsorbed on the samples of the physical pore structure of absorbed water removal of the weight loss. It is worth noting that PET alone pyrolysis weight loss starting temperature is 360°C, PET and co-pyrolysis of coal is not the phenomenon of weightlessness near the temperature, it may be due to: Shenfu coal is lower rank bituminous coal, beginning to softening in 350°C, the product of cracking was absorbed by softening coal, significantly reduces the weight loss rate of PET, in Figure 1, there can be seen from the weight loss curve of the experimental group I, II, III that the weight loss rate of PET and co-pyrolysis of coal were significantly reduced, another reason may be that: the KOH begin to melt under this temperature which absorbed the product of PET pyrolysis, all of that were formed by the experimental group II and VI. This shows that Shenfu coal and KOH may also lead PET to significantly reduced weight loss, products of PET pyrolysis may be completely absorbed, and participate in aromatic polycondensation reaction. Pyrolysis gas chromatography analysis in experimental group I showed that PET pyrolysates have five main product as the table shown in Figure 2, the peak intensity is proportional to the amount generated.

Samples of the FT-IR analysis showed that the carbonyl groups and oxygen-containing heterocyclic broke off and created a large number of CO during charring, aliphatic side chains and low-molecular-weight compounds which based on fat structure cracked and generated gaseous hydrocarbon (such as CH₄, C₂H₄, and C₃H₈, etc.), which explained the phenomenon of macro-weightlessness of samples at 450°C. In this temperature range the bridge-bond in the structure of unit coal such as -CH=CH-, -CH₂=CH₂, -CH₂=O-, -O-, -S-and so on generated free radicals fragment due to heating[5].

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Figure 1 Thermogravimetric analysis curve

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Weight (%)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>100</td>
<td>80</td>
</tr>
<tr>
<td>200</td>
<td>60</td>
</tr>
<tr>
<td>300</td>
<td>40</td>
</tr>
<tr>
<td>400</td>
<td>20</td>
</tr>
<tr>
<td>500</td>
<td>10</td>
</tr>
</tbody>
</table>

1. AC I; 2. AC II; 3. AC III; 4. AC IV; 5. AC V; 6. AC VI

Figure 2 Pyrolysis gas chromatography analysis for PET and the structural formula of products corresponding to the chromatographic peak

1. CH2=CH2, CH3CHO; 2. C6H6; 3. C6H5COOH=CH; 4. C6H5COOH; 5. CH2=CH-OOH-C6H4-COOCH=CH2

The cracking products of PET were absorbed by carbonization system, and the main gases were only CO2, CO, H2, CH4 during the carbonization process (shown in Figure 3), which showed that the cracking products of PET were attacked by thermal alkali and free radicals, and occurred second-cracking and generated CO3, CO, H2, CH4, C2H4 and C6H6. The analysis of main gas component showed that substantial amount of C2H4 and C6H6 were not released, both of which contained weaker π bond and occurred easily electrocyclic reaction under heating, indicating that C2H4 and C6H6 molecules may be captured by coal structure, and participated in the reaction of dehydrogenation and polycondensation in the aromatic structure of coal, the reaction as follows in figure 4.

Figure 5 is the XRD analysis of AC VI that do not any treatment after carbonization. The results show that the main potassium compound formed in the activation process is potassium carbonate, hydrated potash and a spot of potassium oxide and potassium super-oxide. The study of Lozano-Castello D [6-8] shows that potassium carbonate formation does not only take place on the carbon surface to forming a shell that surrounding the carbon particles, but also has molten potassium hydroxide congregate in the pore and holes of carbon. Potassium ion has the strong effect of electron donating and, in the higher temperature, can form the complex salt 'CO-K′ that caused the break of carbon bond, then form the ‘CO-K′ to repeat the catalytic reaction of ‘open-loop-bond breaking-open-loop’. In the condition of above 873K, potassium ion is reduced to atomic state by carbon atoms on the primary formed pore wall and then form the micropore structure after carbon atom released [9-11]. The XRD analysis as Figure 4 also detects that the atomic state of potassium exists.

Figure 3 The analysis of the main gas elements in the carbonization process

Figure 4 The reaction of dehydrogenation and polycondensation in the aromatic structure of coal

The peaks of (002) and (004) due to aromatic ring carbon net synusia in space arrangement degree of orientation. That is, the synusia packing height (Lc). The peaks of (100) and (110) due to the condensation degree of aromatic ring that is the size of the aromatic carbon net synusia (La). The packing number of aromatic plane is about 3 or 4 based on the microcrystalline parameters Lc = 1.16 nm calculated from formula for Bragg, La = 2.38 nm, d(002) = 0.4133nm as a measuring index of
graphitization degree, d(002) is smaller, the degree of graphite will be higher (the limit is d(002) of graphite = 0.3354nm). Studies show that, the d(002) of microcrystalline is higher, the adsorption properties of its production will be better, which explains the high product of methylene blue, as well as provides a micro-structural basis of a good carbonization collaborative effect of coal and PET plastic.

![Graphite XRD Analysis](image)

Figure 5 Shenfu coal/PET Co-carbonization material XRD analysis

4 Conclusions

1) The carbonization cracking of PET can promote the carbonization of Shenfu coal and formation of pore structure. The cracking products of PET were attacked by thermal alkali and free radicals occurred by second-cracking, the products occur the electrocyclic reaction with coal macromolecule. Shenfu coal and PET exists the great co-carbonization synergistic effect.

2) The materials take on disordered state in whole and exist microcrystalline graphite in part. The d(002) is large which results in the increase of the value of methylene blue.

It can provide theoretical foundation of the directional preparation of cheap and high performance activated carbon materials and an effective way for the comprehensive treatment of white pollution, meanwhile, play an active driving role for development and utilization of the high additional value of our national coal resources.

References