Improving the antioxidative ability
of porous carbon by boron-doping

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Introduction

Recently, plenty of researches on carbon’s oxidative reaction and high-temperature oxidation resistance have been made great progress[1-5]. Carbon/carbon composites have been used in the head of missile, the spout of rocket engine, the device of automobile brake and so on[6], but it is very little of the researches on the antioxidation of porous carbon in the high temperature.

Porous carbon is a porous carbonaceous material, with its advantage of resisting acid and alkali, conductivity, heat transfer, abundance of porous structure and surface group, has been widely used in adsorption, separation, catalysis, electronics, energy, chemistry, medication and other fields[7]. Because porous carbon has unique pore structure, surface acidity, mechanical properties and chemical stability, it can be acted as catalyst or the catalytical carrier [8]. In this field, the activated states can be decentralized highly and the reaction heat can be removed promptly by high surface area(S BET), in petroleum refining, agglomeration and coke deposits can be reduced, additionally as the catalytical carrier, the pore diameter and the hydrophilic and hydrophobic properties can be adjusted according to the requirement, and the precious metal can be retrieved by burning of scrap catalysts. However, antioxidative ability of porous carbon is very poor, in the air at 370° porous carbon begins to be oxidated, it directly leads carbon-based material to the weight loss, increasing the resistivity and porosity, and decreasing mechanical properties, so that the use of porous carbon in catalytical fields is restrained[9]. In order to insure the carbon-based material reliability, safety and long service life in the use, antioxidation must be done. The current methods of antioxidation are active point inhibition, coating inhibition and matrix inhibition[10]. In this work, porous carbon has been adopted by the solid boron-doping to improve the oxidation resistance under the high temperature.

Experimental

Materials

Porous carbon as the raw material which is from petroleum coke by KOH chemical activation. Activation condition is 800 in the N 2 atmosphere with KOH /petroleum coke=2.5:1. B 4C is the main composition of boronizing additive and it can provide boron atom during boronizing process.

Modification of porous carbon from petroleum coke by solid boron-doping

Porous carbon (KOH/C=2.5:1) was mixed with additive, and then put the mixture into the reactor in a high-temperature carbonization furnace, the whole process is proceeded in the N 2 atmosphere of 30-40 ml/min, and the temperature is controlled by intelligent temperature instrument, ascend to 850 ° by 10 ° /min, keeping temperature is 5h, heat treatment yield usually is 88%(wt).

Measurement

Weight loss of oxidation

The samples of Porous carbon were heated from 150-750 °, at 150 °, 300 °, 400 °, 500 °, 600 ° and 750°, they were constant temperature 30min respectively, the weight of before and after heated will be recorded and the weight loss after oxidation could be get. The temperature was controlled by the intelligent procedure instrument (CHNT69L9, LONG KOU Advanced Science and Technology company).
TG/DTA
The modified sample was analysed by TG/DTA (TGA92/DSLIII, France SETARAM company).

BET
$S_{\text{BET}}$, pore size distribution and average pore radius were measured by IGA (IGA-001, British HIDEN company) intelligent weight analysis instrument.

Scanning electron microscope (SEM)
Observing the surface shapes of modified porous carbon by the image of SEM (JSM-6360L, Japanese Electron company). And then analyses the sample’s components with the spectrum of XPS.

Catalytic activation of porous carbon
The activity of the molecular sieve catalyst usually is determinated through Microreactive Activation Method (MAT) in the laboratory. Put 5.0g catalyst in the fixed bed subminiature reactor (HPMR-I, China University of Petroleum Instrument factory). Standard material (Dagang 235-337 light diesel) was used, the conditions of MAT are: temperature 460 °C, the weight of space velocity 16h⁻¹, the catalyst/oil 3.2, the reactive time 70s. The percentage of mass of the production ($<204$ gasoline +gas+coke)/(total feed-in material) is catalytical microreactive activation(MA).

Results and Discussions
Antioxidation of porous carbon after boron-doping
Figure 1 shows oxidative weight loss of porous carbon after boron-doping, named PAC1 (raw material named PAC).

Figure 1. The oxidative weight loss of PAC and PAC1
In industrial refining, the temperature of Flow Catalytic Cracking (FCC) is about 400° ~600°, so antioxidation of porous carbon after boron-doping must be more than 600°. In Figure 1 it can be seen that the weight loss rate of porous carbon is down from 70% to 20% at 600°, it suggests that oxidation resistance is obviously improved.
In temperature range 110-900 °C, the percentage of the mass of the samples showed downward trend with the rise of temperature (in figure 2), the PAC was obviously decreasing around 370 °C, after 600 °C the curve became gently. The PAC1 decreased significantly at 550 °C, after 700 °C the curve trended gently. The maximal weight loss rate of PAC1 appeared at about 600 °C compared to PAC at about 350 °C. This indicated the limitation of weight loss rate obviously shifted later after boron-doping. At 600 °C, the weight loss rate of PAC was more than 70% compared to the PAC1 only about 20%, the result was consistent with oxidative weight loss. It also indicated that porous carbon after boron-doping could be suitable for FCC process.

### The change of pore structure of porous carbon and its antioxidative mechanism

The average pore diameter and some characteristics of PAC and PAC1 were analyzed by IGA, which give the information of the porous carbon before and after boron-doping in Table1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET m²/g</th>
<th>Average pore diameter nm</th>
<th>Micropore volume cm³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAC</td>
<td>1527.72</td>
<td>2.314</td>
<td>0.7138</td>
</tr>
<tr>
<td>PAC1</td>
<td>1351.94</td>
<td>2.160</td>
<td>0.6795</td>
</tr>
</tbody>
</table>

The micropore and mesopore distributing of porous carbon before and after boron-doping, which include the information on the change of pore structure of porous carbon show in Figures 3 and 4.
The results indicated that boron-doping is closely related to the pore structure of porous carbon. Obviously boron-doping lead to the infiltration of boron atom so that makes $S_{\text{BET}}$ and pore volume of porous carbon decrease, and changes the pore distribution of porous carbon greatly. Because of the infiltration of boron atom, the quantity of active points on the surface of porous carbon was greatly decreased, prevented porous carbon from being oxidated at high temperature, enhanced the antioxidative ability of porous carbon.

Figures 3 and 4 show the large pore of the modified porous carbon was small amount and the main components were micropore and mesopore, the volume of micropore and mesopore was reducing greatly after boron-doping, it showed that that boron-doping made the density of micropore distribution was deceased from 0.84nm to 0.28nm, the density of mesopore distribution was gradually decreased.

Figures 5 and 6 are SEM morphologies of porous carbon before and after boron-doping (magnification are ×2000).
It can be seen that the surface of PAC was covered with many holes and very rough, the surface holes of PAC1 were reduced obviously and covered with a lot of matters similar to the shape of ball, the active points, holes and cracks of the surface of porous carbon may be blocked, which can prevent the oxidative gas from spreading the surface of porous carbon to the inside, and achieve the purpose of antioxidant ultimately. X-ray photoelectron spectroscopy (XPS) analysis of the PAC1 and PAC2 which the sample’s weight loss rate of PAC1 is 21.25% shows in figure 9.
In Figure 7 the B\textsubscript{1s} peak of the sample PAC2 was 193eV, called B\textsubscript{2}O\textsubscript{3} peak, agree with Cermignani et al.'s\cite{11-12} study. The peak of the PAC1 was a little wide, and the highest point was near to 186.5eV, this peak was considered as the substitutive boron\cite{13}. Jacques et al\cite{14} believed that the 188.8eV corresponding peak was considered as the substitutive boron in graphite’s structure, the peak at 188.1ev was B\textsubscript{4}C\textsubscript{1-x}, for 186.5eV peak was boron beam in Shirasaki et al.'s work\cite{15}.

XPS analysis clearly confirmed the formation of B\textsubscript{2}O\textsubscript{3}, the deposition of B\textsubscript{2}O\textsubscript{3} significantly reduced the oxidative rate of porous carbon\cite{15-21}, Therefore, the form of B\textsubscript{2}O\textsubscript{3} thin layer on the surface of porous carbon was the main mechanism to improve the oxidation resistance \cite{22}. Even if the deposition of B\textsubscript{2}O\textsubscript{3} can not form continuous thin layer on the surface of carbon, still there was a little B\textsubscript{2}O\textsubscript{3} in the form of beam scattered on the active points of the surface of porous carbon and closely integrated with the carbon atom, there by shielding the active points, improving the oxidation resistance\cite{19}. The oxidation resistance of modified porous carbon is due to the shielding of the active sites on the surface of B\textsubscript{2}O\textsubscript{3}. The results of XPS show that boron as a dopant was substituted, and boron-doping was a substituent and forming solid soluble substance with porous carbon.

**The MA of porous carbon before and after boron- doping**

The MA of PAC and PAC1 was listed in Table 2. For FCC, the balanceable catalytical activation of zeolite molecular sieve is about 60-70\%\cite{23}, the MA of PAC and PAC1 reached 88.14 and 70.25\% respectively, although the oxidation resistance of modified porous carbon is reduced, and compared with the traditional zeolite molecular sieve, it still has its predominance, moreover, the ability of oxidation resistance of the modified porous carbon is enhanced significantly, as the catalyst porous carbon could meet the demands of the industry. The catalytic activation of porous carbon is related with its S\textsubscript{BET} under normal circumstances, the larger the S\textsubscript{BET}, the higher the catalytical activation is. And the catalytical activation of porous carbon is also closely related to the distribution of pore size.

**Table 2  The MA of PAC and PAC1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET m\textsuperscript{2}/g</th>
<th>Total pore volume cm\textsuperscript{3}/g</th>
<th>Micropore volume cm\textsuperscript{3}/g</th>
<th>MA %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAC</td>
<td>1527.72</td>
<td>0.8794</td>
<td>0.7138</td>
<td>88.14</td>
</tr>
<tr>
<td>PAC1</td>
<td>1351.94</td>
<td>0.7318</td>
<td>0.6795</td>
<td>70.25</td>
</tr>
</tbody>
</table>

The results indicate that the high specific surface area of porous carbon has a high catalytical activation for FCC, and this is different from FCC carbon positive ion reactive mechanism. Porous carbon which was from KOH...
chemical activation does not have a strong acidity which is demanded by cracking reaction, therefore it should not 
occur the cracking, but in fact it occurred. The explanation may be the micropore of porous carbon plays a decisive 
role. The micropore of porous carbon is in the range of Nanosize and has the same size as molecular. This micropore 
also is called Nanospace that has some special functions which other some larger pores generally are not available, it 
is not only the adsorptive space but also the reactive space, it often is considered as a specially functional reactor. In 
this reactor some unexpected reactions could often be occurred.

For FCC the catalytical activation of high $S_{\text{BET}}$ of porous carbon is due to Nano-characteristics, this needs 
further be studied.

Conclusions

(1) At 600 $^\circ$C, compared with PAC1 the weight loss rate of PAC was down from 70% to 20%.

(2) After boron-doping, both total pore volume and micropore volume of porous carbon are a downward trend, 
the $S_{\text{BET}}$ of porous carbon decreased 10-20%, the micropore and mesopore of porous carbon have some losses in 
different degrees.

(3) Compared with PAC, although the $S_{\text{BET}}$ and the MA of PAC1 are slightly lower, the MA of PAC1 still 
reaches 70.25, the antioxidative ability has been improved obviously around 600 $^\circ$C after boron-doping.

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