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 alkli, 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 refinning, agglomeration and coke deposits can be reduced, additional 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 $150-750^o$, 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_{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 determined 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 , the weight of space velocity $16h^{-1}$, the catalyst/oil 3.2, the reactive time 70s. The percentage

of mass of the the production（ <204 gasline +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).
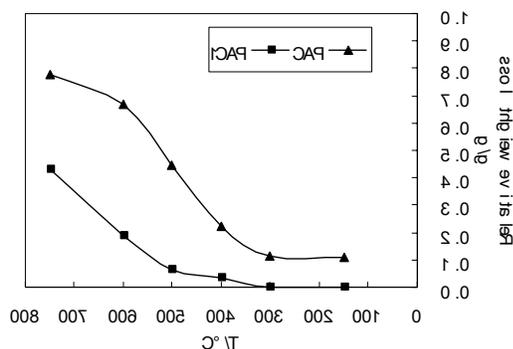

Figu re 1. The oxidative weight loss of PAC and PAC1

In industrial refinning, the temperature of Flow Catalytic Cracking (FCC) is about $400^{\circ} \sim 600^{\circ}$, 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.
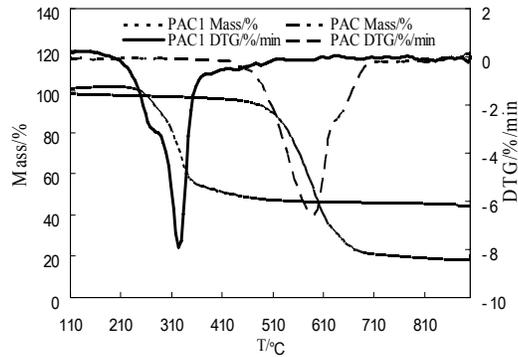
Figure 2. The themal weight loss of PAC and PAC1

In temperature range 110-900°, 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°, after 600° the curve became gently. The PAC1 decreased significantly at 550°, after 700° the curve trended gently. The maximal weight loss rate of PAC1 appeared at about 600 compared to PAC at about 350°. This indicated the limitation of weight loss rate obviously shifted later after boron-doping. At 600°, the weight loss rate of PAC was more than 70% compared to the PACl 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.
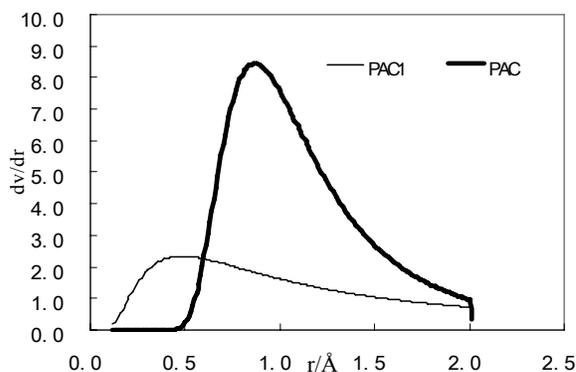
The change of pore structure of porous carbon and its antioxidative mechanism

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

Table 1 Some characteristics of PAC and PAC1

Sample	BET m^2/g	Average pore diameter nm	Micropore volume cm^3/g
PAC	1527.72	2.314	0.7138
PAC1	1351.94	2.160	0.6795

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.

**Figure 3** The distribution of the micropore of PAC and PAC1
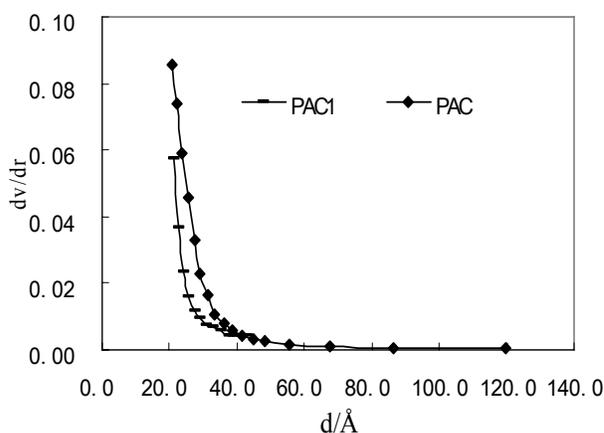
**Figure 4**   The distribution of the mesopore of PAC and PAC1

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_{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).
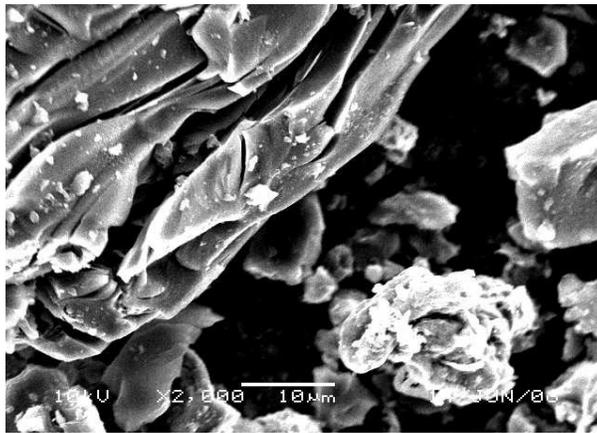
Figure 5 SEM morphologies of PAC
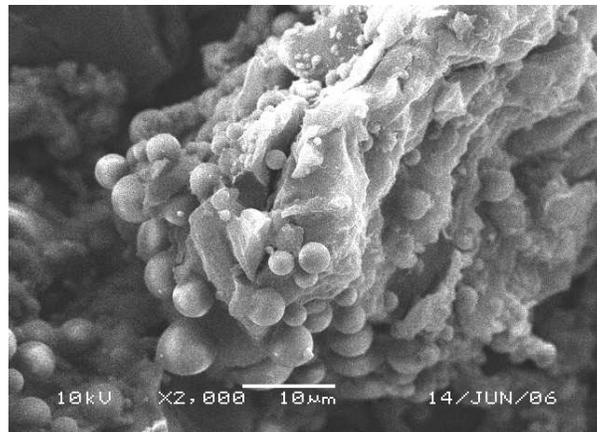
Figure 6　SEM morphologies of PAC1

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.
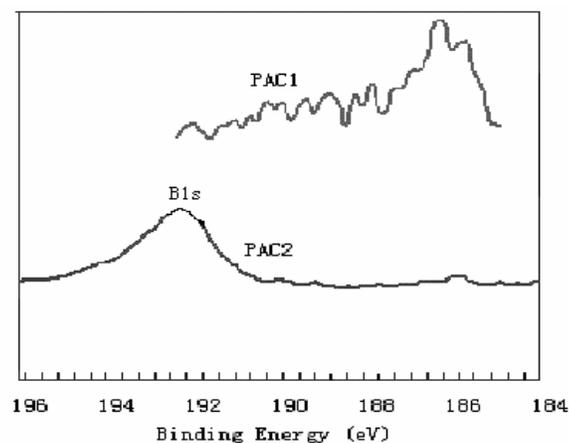
Figure7 The XPS of PAC1 and PAC2

In Figure 7 the B_{1s} peak of the sample PAC2 was 193eV , called B_2O_3 peak, agree with Cermignani et al's[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[13]. Jacques et al[14] believed that the 188.8eV corresponding peak was considered as the substitutive boron in graphite's structure, the peak at 188.lev was B_XC_{1-X}, for 186.5ev peak was boron beam in Shirasaki et al's work [15].

XPS analysis clearly confirmed the formation of B_2O_3, the deposition of B_2O_3 significantly reduced the oxidative rate of porous carbon[15-21], Therefore, the form of B_2O_3 thin layer on the surface of porous carbon was the main mechanism to improve the oxidation resistance [22]. Even if the deposition of B_2O_3 can not form continuous thin layer on the surface of carbon, still there was a little B_2O_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[19]. The oxidation resistance of modified porous carbon is due to the shielding of the active sites on the surface of B_2O_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%[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_{BET} under normal circumstances, the larger the S_{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

Sample	BET m²/g	Total pore volume cm³/g	Micropore volume cm³/g	MA /%
PAC	1527.72	0.8794	0.7138	88.14
PAC1	1351.94	0.7318	0.6795	70.25

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_{BET} of porous carbon is due to Nano-characteristics , this needs further be studied.

Conclusions

(1) At 600 , 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_{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_{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   after boron-doping.

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