

INVESTIGATION OF PREPARATION PROCESS FOR POROUS CARBON WITH SUPER-HIGH SURFACE AREA

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Introduction

Petroleum coke is a material of low volatility produced during the refining of crude oil and generally comprises carbonaceous material including elemental carbon, as well as relatively heavy hydrocarbon products including straight- and branched-chain saturated and unsaturated hydrocarbons, cyclic and polycyclic saturated and unsaturated hydrocarbons, whether unsubstituted or substituted with acyl, cyano, sulfur, or halogen constituents, and organometallic compounds. It is abundant and cheap, being widely used as fuels and for the production of graphite electrodes in electric furnace smelting.

A new value-added carbon product, porous carbon with super-high surface area, is developed from petroleum coke, which can be widely used as nature gas adsorbent, microwave absorbent and, after pore structure modification, PSA adsorbent for gas separation.

Experimental

1. Preparation of porous carbon with super-high surface area

Porous carbon were prepared from petroleum coke (manufactured by ShengLi-Refinery) which mainly consists of carbon atoms, more than 90%,

with minor other atoms such as S, N and heavy metal. The raw material, hard, compact and non-porous, was grounded and sieved from 100 ~ 200 mesh. The activator ^[1,2] is prepared by mixing, slurring and stabilizing the alkali metal hydroxide or oxide with other transition metal chlorides or nitrates. Petroleum coke powder was chemically activated using alkali metal hydroxides or oxides as the reagent, acetone or ethanol as the surfactant. Activated agent, acetone and water were added in specific amounts to petroleum coke. The mixture was stirred homogeneously, giving slurry. The activation of petroleum coke was then carried out in a parallel stainless steel reactor at a certain temperature. The effects of activation temperature, holding time and activated agent ratio on surface area and pore structure of the carbon produced in our lab were investigated. After activation, the sample was submerged in deionized water, filtered and then rinsed again in deionized water to remove any activator derivatives.

2. Characterization of porous carbon with super-high surface area

The surface properties such as surface area, average pore diameter and pore volume were determined using an automatic ASAP2010

apparatus (Micromeritics, USA) by N₂ absorption at 77.3K.

The surface elemental composition of carbon molecular sieve was determined by energy distribution spectrum using X-ray microanalysis (ISIS, Oxford Instrument).

2. *In-situ* TG-DTA test on preparation process

TG-DTA test was performed with a WCT-2 work station (Peking instrument company, China) at a programmed temperature velocity of 10K/min in N₂ with flow rate of 25ml/min. The prepared mixture of petroleum coke and activator was placed in the reacting tube with activating temperature rising from about 323K to 1273K.

Results and discussion

1. The effects of activating conditions on pore structure of porous carbon

(1) Effects of activated agent ratio on structure variation of porous carbon

Porous carbons were prepared by chemical activation using various amounts of activated agent. Pore structure of the carbons was determined using an automatic ASAP2010 apparatus by N₂ absorption at 77.3K. A quantitative comparison of the variation of the textual structure, mesopore and micropore distribution of the carbons is given in Table 1.

The results show that specific surface area, average pore size, average micropore size and pore volume in different size range are obviously increased with increasing use of activator. It means that the amount of activator used determines the depth of activation. The more activator is used, the more micropores are developed. It can be seen from Table 1 and Figure 1 that the volume of pore range

from 0.7 to 3nm takes up about 90% in the total pore volume. The absorption isotherms of all porous carbons shown in Figure 1(c) belong to typical type I isotherm^[3], which also indicates that the porous carbons are microporous carbon-based materials. The corresponding relative pressures of the inflexions of the isotherms are also increased with increasing use of activator, which indicates that the average micropore size becomes larger with the use of more activator.

(2) Effects of activating temperature on structure variation of porous carbon

Petroleum coke was activated at different temperature, which resulted in the variation of pore structure for porous carbons. Table 2 shows that specific surface area, pore diameter and pore volume all change to be larger with the rise of activating temperature. Obviously, the mesopore (>2nm) volume increases more substantially than the micropore volume. It should be also noted that a shorter period is demanded for activation at high temperature. Excessively long period of heat retaining at high temperature may be responsible for the deviation of activating results at 1173K. Too long holding time at high time may destroy micropore structure and result in the decrease of specific area.

2. *In-situ* TG-DTA study of preparation process

In-situ TG-DTA study of preparation process is shown in Fig.2. As it can be seen, the TG spectrum can be split into three steps: <473K, 473~873K and >873K. A viewpoint is tentatively proposed, weight loss below 473K resulting from desorption of physisorbed H₂O, weight loss between 473~873K resulting from dehydration of activator and weight loss above 873K resulting from

gasification of carbon atoms in framework in terms of carbonous oxide, which can be testified by structure characterization (in Table3) of products with different ultima elevated temperature.

There being hardly porestructure below 773K, micropore structure is mainly formed higher than 873K, which is corresponding to the weight loss above 873K in TG-DTA profile. When elevated temperature is about 1073K, the rate of formation of mesopore was accelerated dramatically. Therefore, activating temperature is the dominating factor to micropore-forming reaction. Optimum activating temperature should be range from 873K to 1073K.

During the process of activation, surface oxides were formed or decomposed remarkably on the surface of carbon, which was demonstrated by EDX analysis of carbon products with different ultima elevated temperature. The O/C atomic ratio on the surface of carbon were 0.2625, 0.5453, 0.3930 with respect to products with ultima elevated temperature at 873K, 973K and 1073K respectively. FT-IR spectra also show the presence of C=O and O-H species in carbon products.

Conclusions

- (1) Activated agent ratio, activated temperature and holding time have much influence on the structure of the porous carbons;
- (2) Activating temperature is the dominating factor to micropore-forming reaction. Optimum activating temperature should be range from 873K to 1073K.

References

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2. Takahiro, Kasuh, Guhji, Morino. US, 92 5143889. 1992
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Table 1. The effects of activating agent ratio on pore structure of porous carbons

W_{ACT}/W_{Coke}^b	BET surface area m ² /g	Average pore diameter nm	Average micropore diameter nm	Pore volume (~2nm) cm ³ /g	Pore volume (2nm~) cm ³ /g
1	909	2.07	0.81	0.36	0.07
2	1174	2.12	0.83	0.40	0.19
3	2274	2.10	0.88	0.64	0.58
5	2860	2.15	0.88	0.76	0.80

^a Activating conditions: activating temperature=1073K, retaining time=60min, the rate of elevating temperture=10K /min, N₂ flow rate=30ml/min;

^b W_{ACT}/W_{coke} : weight ratio of activator vs. coke.

Table 2 The effects of activating temperature on pore structure of porous carbons

Activating temperature	Retaining time	BET surface area	Average micropore diameter	Pore volume (~2nm)	Pore volume (2 nm ~)
<u>K</u>	<u>min</u>	<u>(m²/g)</u>	<u>(nm)</u>	<u>cm³/g</u>	<u>cm³/g</u>
973	60	1827	0.85	0.60	0.33
1073	60	2859	0.88	0.76	0.80
1173	30	3149	0.89	0.82	1.64
1273	0	3469	0.91	0.92	1.76

^a Activating conditions: $W_{ACT}/W_{coke}=5$, the rate of elevating temperature=10K /min, N_2 flow rate=30ml/min.

Table 3. Structure characterization of carbons with different ultima elevated temperature

Ultima elevated temperature	BET surface area	Average micropore diameter	Pore volume (~2nm)	Pore volume (2 nm ~)
<u>K</u>	<u>(m²/g)</u>	<u>(nm)</u>	<u>cm³/g</u>	<u>cm³/g</u>
773	3	none	none	0.01
873	462	0.76	0.20	0.03
973	1023	0.80	0.41	0.08
1073	1737	0.85	0.57	0.31

^a Activating conditions: $W_{ACT}/W_{coke}=5$, the rate of elevating temperature=10K /min, N_2 flow rate=30ml/min

The reactor was taken out from stove and refrigerated as soon as temperature was up to target value.

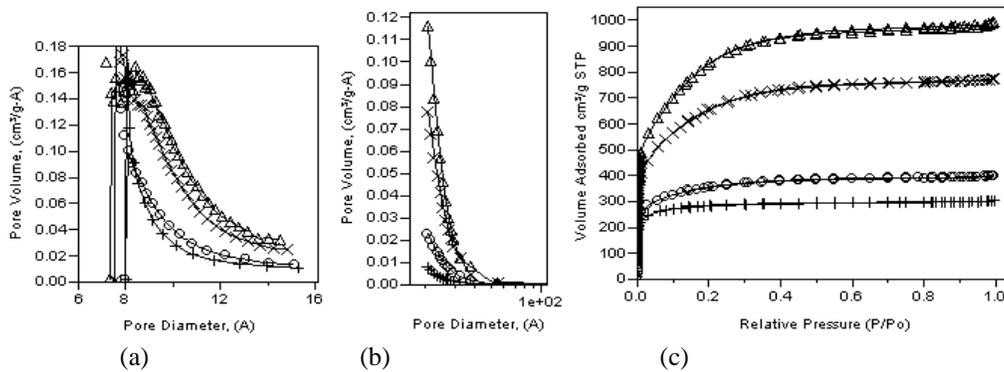


Figure 1. Characterization of pore structure of porous carbons

(a): micropore distribution; (b): mesopore distribution; (c): absorption isotherm

+ : $W_{ACT}/W_{coke}=1:1$; o : $W_{ACT}/W_{coke}=2:1$; x : $W_{ACT}/W_{coke}=3:1$; Δ : $W_{ACT}/W_{coke}=5:1$

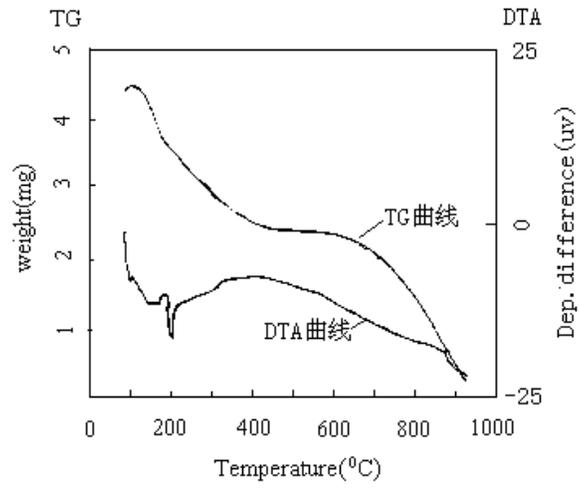


Figure 2. *In-situ* TG-DTA spectra of preparation process for porous carbon