

PREPARATION OF CARBON MOLECULAR SIEVES FROM PETROLEUM COKES

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Introduction

Carbon molecular sieves (CMS) have been synthesized from petroleum cokes manufactured by Shengli Refinery which mainly consists of carbon atoms, more than 90%, with other atoms such as S, N and heavy metal. The raw material is hard, compact and non-porous. A new carbon product, a novel multifunctional carbon molecule sieve, is developed from petroleum coke, which can be widely used in environmental and petrochemical industry. Petroleum coke powder was chemically activated using alkali potassium hydroxides or oxides as the reagent and pyrolytically modified with methane or liquefied petroleum gas (LPG). The activation of petroleum coke was then carried out in a parallel stainless steel reactor at a certain temperature. The product is expected to use as adsorbent for air separation in pressure swing adsorption (PSA) process. The prepared carbon molecular sieves with high specific areas and uniform and narrow micropore distribution are ideal materials for PSA operation.

Experimental

The preparation procedure is as followed:

The raw material was grounded and sieved to 20 ~ 40 mesh. The mixture of coke and activation agent was stirred homogeneously. The pre-oxidation and

activation of petroleum coke was then carried out in a parallel stainless steel reactor at a certain temperature with KOH activation agent of 1.5:1 of cokes in nitrogen flow of 20ml/min. The effects of activation temperature, holding time and activated agent ratio on surface area, pore structure of the carbon produced were investigated. The resulted carbon precursor has been kneaded with sulphate pulp waste liquor and extruded to 2mm cylindrical pellets. After drying, these pellets have been carbonized in the same oven for 30 minutes at 1073K, impregnated, washed and dried. Finally, carbon deposition has been performed through the cracking of methane or liquid petroleum gas. Optimized operating condition of carbon deposition is still investigated, including cracking temperature, cracking time and gas velocity and so on. By now, product with micropore diameter 5.8Å and micropore volume 0.4cm³/g has been attained. The micropore structure characterization is performed using nitrogen adsorption in 77K in a Micromeritics ASAP2010 system. The micropore size distribution is calculated by HK method. The air separation performance will be evaluated in a small single PSA apparatus.

Result and discussion

Preparation condition and BET surface area of four sample is listed in table.1.

CO₂ activation has little effect on the condensed material while the behavior KOH is remarkable. The mechanism of KOH activation was illustrated elsewhere [1]. It is speculated that CO₂ hardly enters the interstice of crystalline and work because there is no primary pore in coke structure. Moreover the severe weight loss of CO₂-KOH-coke after activation is in agreement with above speculation, for CO₂ might enter the interior of coke through the porous network which KOH creates and the activation condition then was too rigorous for CO₂ activation. Meanwhile it indicated that the same activation degree could be perhaps attained at the lower consumption of KOH if KOH activation is combined with CO₂ activation and the other condition is optimized.

The BET surface area is reduced sharply when the amount of KOH was reduced slightly. It is suggested the addition of KOH play an important role.

Petroleum coke was pre-oxidized at 573K for 4 hours in air prior to activation. It shows that the variation of pore structure on carbon molecular sieves caused by preoxidation. Of interest is that mesopore (>20Å) volume decreases remarkably due to preoxidation. The decrease of mesopore (>20Å) volume results in increase of density for carbon molecular sieves, which is meaningful for PSA operation. Moreover, it provides a possible way to produce carbon molecular sieve with uniform and narrow micropore size distribution.

The carbon deposition results of two kinds of precursor are compared, as shown in table.2 and figure 1 to 4. AC is commercial activated carbon and KOH-coke is the same one in table.1. 'CD' in bracket indicates that the sample has been carried out carbon deposition.

After the carbon deposition, the micropore size of AC was slightly reduced at the cost of surprisingly loss of the micropore volume. On the other hand, the micropore size of KOH-coke was obviously

reduced while the micropore volume keep unchanged and the pore size distribution is very narrow.

Comparing the properties of the two kinds of precursor before carbon deposition, it was found the micropore size distribution of KOH-coke was sharp and micropore was majority. So precursor with abundant and uniform micropore system is preferential.

Conclusion

1. The cheap condensed petroleum cokes have been successfully used as starting material of costly CMS.
2. KOH activation is combined with CO₂ activation might be resulted in commercial process to produce CMS precursor.
3. The adsorption isotherms of carbon molecular sieves is representative typical type I.
4. The micropore size (<1nm) of the precursor might be further modified to produce 0.58nm CMS without the obvious loss of micropore volume.
5. The micropore size of KOH-coke precursor was obviously reduced while the micropore volume keep unchanged and the pore size distribution is very narrow after carbon deposition with methane or LPG.

Reference

1. Brenda K.C.Chan, K.Mark Thomas, and Harry Marsh. The interaction of carbons with potassium. Carbon 1993; 31(7):1071~1082.
2. W. Xing, Z.-F. Yan, Synthesis and characterization of a novel multifunctional carbon molecular sieve, reprint of 220th ACS national meeting, Division of fuel chemistry, 2000, 527.

Table.1 the result of activation

	Coke	CO ₂ -Coke	KOH-Coke	CO ₂ -KOH -Coke
BET Surface (cm ² /g)	4.8258	6.8966	1522.8648	206.3436
Preparation Condition		CO ₂ 160cm ³ /min 1073K 30min	KOH Coke Wt =1.5 1 1123K 120min	KOH Coke Wt =1.2 1 CO ₂ 160cm ³ /min 1123K 120min

Table.2

	BET Surface	Single Point Total Pore	HK Maximum	Median Pore
	Area(cm ² /g)	Volume(cm ³ /g)	Pore Volume(cm ³ /g)	Diameter(A)
AC	2055.6540	1.126325	0.541261	8.7665
AC CD	1291.5239	0.730426	0.338806	8.6475
KOH-Coke	1522.8648	0.782067	0.524362	8.2613
KOH-Coke-(CD)	1521.8719	0.688417	0.400155	5.8616

Carbon deposition was performed by the cracking of methane for 40 minutes at ~80cm³/min and 1095K.

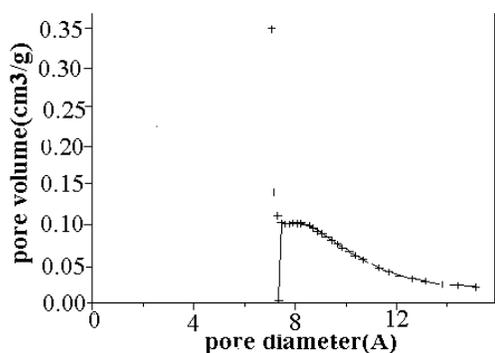


figure1. H-K internal pore volume plot of AC

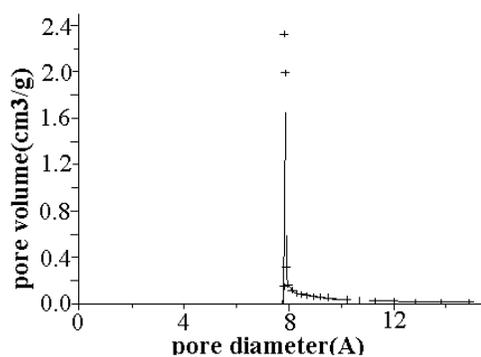


figure2. H-K internal pore volume plot of AC(CD)

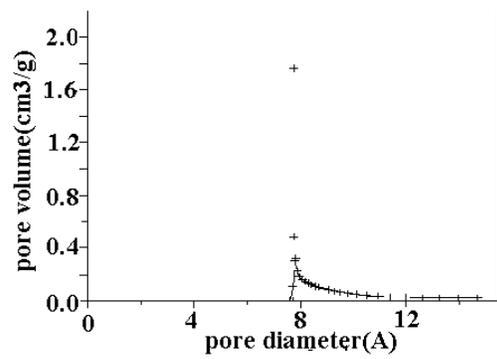


figure 3. H-K internal pore volume plot of KOH-coke

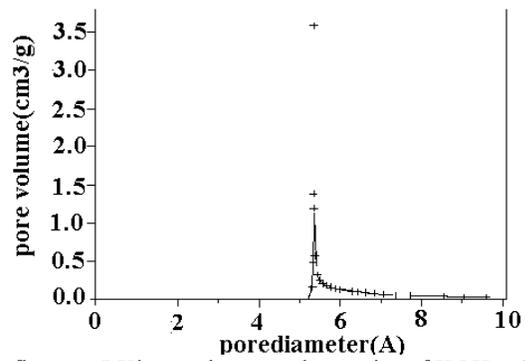


figure 4. I-K internal pore volume plot of KOH-coke(CD)