

# SYNTHESIS AND CHARACTERIZATION OF A NOVEL MULTIFUNCTIONAL CARBON MOLECULAR SIEVE

Wei XING and Zi-Feng YAN\*

*State Key Laboratory for Heavy Oil Processing,  
University of Petroleum, Dongying 257061, P R China*

**ABSTRACT** Carbon molecular sieves were prepared from petroleum coke by chemical activation. The effects of activation temperature, holding time, preliminary treatments and activated agent ratio on surface area, pore structure of the carbon molecular sieves produced in our lab were investigated. The specific surface area and average pore size of the carbon are obviously increased with increasing use of activator and rise of activating temperature. The rate of elevating temperature is not specifically limited. But the heat-retaining time has much influence on the performance of the activated carbon. Suitable holding time may lead to high degree of activation, with result of increase in pore diameter of micropore and mesopore. But too long holding time can destroy pore structure and result in decrease of specific area. In addition, the effects of coke pre-oxidation on activating results were also investigated. Coke pre-oxidation leads to a remarkable decrease of mesopore volume. The carbon molecular sieves prepared in our lab are about 3000 m<sup>2</sup>/g in BET specific area. Diffraction peaks in XRD patterns indicate the generation of a new crystalline phase of carbon. The prepared carbon molecular sieves with extremely high specific area and uniform micropore distribution are ideal materials for natural gas adsorption storage as vehicular fuel. Carbon molecular sieves differing in BET surface area were used to evaluate the natural gas storage capacity on them at different pressures by two-vessel volumetric method at 293 K and up to 5.0 MPa. In addition, this kind of carbon molecular sieve can also be used as microwave absorbent and PSA adsorbent for gas separation.

**KEYWORDS** Carbon molecular sieve, natural gas absorption, chemical activation

## 1. 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, a novel multifunctional carbon molecular sieve, is developed from petroleum coke, which can be widely used as natural gas adsorbent, microwave absorbent and, after pore structure modification, PSA adsorbent for gas separation.

## 2. EXPERIMENTAL

### 2.1 Preparation of Carbon Molecular Sieve

Carbon molecular sieves 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 metals. The raw material, hard, compact and non-porous, was grounded and sieved from 100 ~ 200 mesh. The activator is prepared by mixing, slurring and stabilizing an 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, and 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, preliminary treatments and activated agent ratio on surface area, pore structure, and methane storage capacity of the carbon produced in our laboratory were investigated. After activation, the sample was submerged in deionized water, filtered and rinsed again in deionized water to remove any activator derivatives.

In addition, the pre-oxidation of the coke powder on activating results was also investigated. The coke powder was oxidized in air at 473K for 24 hours prior to activation.

\* To whom correspondence should be addressed-mail: [zfyancat@sunctr.hdpu.edu.cn](mailto:zfyancat@sunctr.hdpu.edu.cn)

## 2.2 Characterization of Carbon Molecular Sieve

The surface properties such as surface area, average pore diameter and pore volume were determined using an automatic ASAP2010 apparatus (Micromeritics) by  $N_2$  adsorption at 77.5K. The total pore volume,  $V_t$ , is derived from the amount of adsorption at a pressure relatively close to unity, given that the pores were totally filled with the liquid adsorbate. The mesopore distribution curve is obtained from the adsorption branch of the  $N_2$  isotherm by BJH method. The micropore distribution is calculated from the gas adsorption using the Horvath-Kawazoe equation, with relatively pressure ( $P/P_0$ ) below 0.01. Adsorption isotherms of  $CH_4$  have also measured by two-vessel volumetric method in a high-pressure range (0–5.0MPa) at ambient temperature.

A BDX-3200 X-ray powder diffractometer, manufactured by Peking University Instrument Factory, was used to identify the crystal form of carbon molecular sieve. Anode Cu  $K\alpha$  (40kV, 20mA) was employed as the X-ray radiation source, covering  $2\theta$  between  $20^\circ$  and  $120^\circ$ . The XRD patterns were monitored and processed by a computer.

The surface morphology of carbon adsorbents was observed using scanning electron microscopy (JEM 5410LV, JEOL Technologies) with the accelerating voltage of 25kV. The surface elemental composition of carbon molecular sieve was determined by energy distribution spectrum using X-ray microanalysis (ISIS, Oxford Instrument).

## 3. RESULTS AND DISCUSSION

### 3.1 Pore Structure Variation of Carbon Molecular Sieve

#### (1) Effect of Activated Agent Ratio on Structure Variation of Carbon Molecular Sieve

Carbon molecular sieves were prepared by chemical activation using various amounts of activated agent. A quantitative comparison of the variation of the textural structure, mesopore and micropore distribution of carbon molecular sieves 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 is obviously increased with increasing use of activator. It means that the amount of activator used determine 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 7 to  $30\text{\AA}$ , which is believed to play a role for natural gas adsorption in relatively low pressure, takes up about 90% in the total pore volume. The adsorption isotherms of all carbon molecular sieves shown in Figure 1(b) belong to typical type I isotherm, which also indicates that carbon molecular sieve is a microporous carbon-based material.

#### (2) Effect of Activating Temperature on Structure Variation of Carbon Molecular Sieve

Petroleum coke was activated at different temperature, which resulted in the variation of pore structure for carbon molecular sieve. 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 ( $>20\text{\AA}$ ) 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 activation results at 1173K. It may destroy micropore structure and result in the decrease of specific area.

#### (3) Effect of coke preoxidation on Structure Variation of Carbon Molecular Sieve

Petroleum coke was preoxidized at 573K for 24 hours in air prior to activation. Table 3 shows the variation of pore structure on carbon molecular sieves caused by preoxidation. We can draw a conclusion from Table 3 that mesopore ( $>20\text{\AA}$ ) volume decreases remarkably due to preoxidation. The decline of mesopore volume range from  $20\text{\AA}$  to  $30\text{\AA}$  may be disadvantageous for natural gas absorptive storage. However, the decrease of mesopore ( $>20\text{\AA}$ ) volume results in increase of density for carbon molecular sieves, which is meaningful for natural gas storage.<sup>[1]</sup> More importantly, it provides a possible way to produce carbon molecular sieve with uniform micropore-size distribution.

### 3.2 XRD Characterization

Natural gas is absorbed in the micropores that is close related to the crystal structure of carbon molecular sieve. Understanding the crystal structure of carbon molecular sieve is instructive not only for structural optimization of adsorbents prepared, but also for the accurate evaluation BET, porosity, etc., of adsorbents.

The major crystalline phases of carbon molecular sieve were examined by XRD and the spectra were presented in Figure 2. There are 4 sharp peaks visible, which can be indexed as (100, 111, 200, 210) of a primitive cubic unit cell with a unit cell length of  $2.026\text{\AA}$ . Assuming a disordered rhombohedral (hexagonal) cell, this calculates to  $a = 1.43$  and  $c = 3.51\text{\AA}$  which is comparable to the distances in graphite,  $3.35\text{\AA}$ , within and perpendicular to the layers. Although

how the carbon crystal lattice arranges to form this centralized distribution of micropore is not known exactly, it is a really interesting point worth further studying. It may be the fundamental to understand the nature of gas absorptive storage on carbon.

### 3.3 SEM and EDX Analysis

The microscopic appearance observation of the carbon was conducted using scanning electron microscopy. The micrographs of absorbents, derived from raw coke and preoxidized coke respectively, are illustrated in Figure 3, from which the porous structure of absorbents is clearly imaged. The markedly different surface morphology between these two absorbents indicates various reacting processes during activation. The pore shapes of absorbents prepared from raw coke look randomly, while the pore shapes prepared from preoxidized coke are circular universally. Although the formation mechanism of these circular pores is not known exactly, it is believed to be close relative with retarding the formation of mesopore, which is reflected in Table 3. After preoxidation at 473K in air for 24 hours, surface oxides generated on the surface of the coke. During activation, these surface oxides removed primarily to form rudimentary pores, which is reckoned to be in favor of subsequent activation.

The surface elemental composition of the absorbents was also characterized by energy distribution spectra using X-ray microanalysis and the results show that carbon atoms accounted for absolute majority on the surface of absorbents with only a small quantity of other atoms such as oxygen, potassium and iron.

### 3.4 Evaluation of Natural Gas Adsorption on Carbon Molecular Sieve

Instability in the oil markets and increase in environmental concerns have stimulated research for alternative transportation fuels. One alternative to gasoline is natural gas, which consists primarily of methane (85% ~ 95%) with minor amounts of ethane, other higher hydrocarbons, and carbon dioxide. The advantage of natural gas is that it is cheaper than gasoline and readily available in the world. Natural gas burns more cleanly than gasoline, emitting fewer toxic hydrocarbons and 90% less carbon monoxide. At present, many governments are actively making efforts to popularize natural gas-driven vehicles, mainly driven by compressed natural gas (CNG), in big city to alleviate the pollution caused by exhaust gas.

The use of natural gas as vehicular fuel, an application where storage volume is limited, has necessitated the use of high-pressure storage, which requires high pressure (20 ~ 30MPa) and an expensive multi-stage compression facility, to give an adequate if not entirely satisfactory driving range. Numerous vehicles have been adapted to use compressed natural gas (CNG) as fuel, which is stored in heavy steel cylinders. The net deliverable capacity for CNG at 1.35 atm (5 psi) is 215 standard liter per liter of storage volume. The disadvantages of such high pressures have stimulated research into the use of absorbents in an attempt to provide a similar energy density, but at relatively low pressure (typical target of 3.4 MPa, 500 psi) achievable by single-stage compression. This concept of absorbed natural gas (ANG) can reduce the highest storage pressure so those lightweight cylinders can be used. The key question is whether the net deliverable capacity of such a device can match or exceed that of CNG. Obviously, one needs a high pore volume, high surface area absorbent for this purpose. This kind of novel carbon molecular sieve produced in our laboratory is such material suitable for the application of ANG.

From above data, derived from characterization of the absorbents in previous sections, it is clear that BET surface area varies with other structural parameters, such as average pore size and microporosity, in direct proportion. Therefore, absorbents differing in BET surface area were used to evaluate the natural gas storage capacity on them by two-vessel volumetric method at 293 K and up to 5.0 MPa. Table 4 submits natural gas storage capacity on absorbents at different pressures. As seen from Table 4, with the increase of storage pressure and BET surface area, natural gas storage capacity enhanced obviously. Of interest is that, with the rise of storage pressure from 3 MPa to 5 MPa, the net increased storage capacity on an absorbent with high BET surface area is large than the one with low BET surface area. Under higher pressure, more relatively large pores play a role in natural gas absorption. Absorbents with higher surface area have more large micropores and small mesopores (20~30Å), which contribute more to natural gas absorption under high pressure than low pressure.

## 4. CONCLUSIONS

- (1) Activated agent ratio, activated temperature and holding time have much influence on the structure of the Carbon Molecular Sieve;
- (2) Coke preoxidation results in the remarkable decrease of mesopore volume;
- (3) A new crystal phase is formed during activation process;
- (4) Increase in pressure from previously suggested 3.4 MPa<sup>[2]</sup> to 5.0 MPa, at which relatively larger pores play a role in natural gas absorption, does allow a greater amount of natural gas to be absorptively stored on the absorbents with high surface area.

This kind of carbon molecular sieve can also be used as microwave adsorbent and PSA adsorbent for gas separation. We are extending study to these areas.

## ACKNOWLEDGEMENTS

Financial supports by the Sheng-Li oilfield and Young Scientists Award Foundation of Shandong Province and Young Scientists Innovation Foundation of China National Petroleum Corporation are gratefully acknowledged.

## REFERENCES

1. Matranga K. R. and Myers A. L. Glandt E. D., *Chem. Eng. Sci.* **1992**, 47, 1569.
2. Quinn D. F. and Macdonald J. A., *Carbon.* **1992**, 30, 1097.

**Table 1.** Characterization of carbon molecular sieve structure

$W_{ACT}/W_{COKE}$	$S_{BET}$ ( $m^2/g$ )	D ( $\text{\AA}$ )	$D_{micro}$ ( $\text{\AA}$ )	V (~20 $\text{\AA}$ ) $cm^3/g$	V(20-30 $\text{\AA}$ ) $cm^3/g$	V(30 $\text{\AA}$ -) $cm^3/g$
1	909.3	20.748	8.077	0.356	0.040	0.029
2	1173.9	21.173	8.267	0.403	0.131	0.062
3	2273.5	21.048	8.786	0.636	0.428	0.150
5	2859.5	21.501	8.857	0.762	0.604	0.201

\*D: average pore diameter  $D_{micro}$ : average micropore diameter  
 $W_{ACT}/W_{COKE}$ : weight ratio of activator vs. coke

**Table 2.** Characterization of carbon molecular sieve structure

T (K)	t (min)	$S_{BET}$ ( $m^2/g$ )	D ( $\text{\AA}$ )	$D_{micro}$ ( $\text{\AA}$ )	V (~20 $\text{\AA}$ ) $cm^3/g$	V(20-30 $\text{\AA}$ ) $cm^3/g$	V(30 $\text{\AA}$ -) $cm^3/g$
973	120	2257.9	20.311	8.688	0.697	0.212	0.078
1073	60	2859.5	21.501	8.857	0.762	0.604	0.201
1173	60	2304.8	23.602	9.106	0.585	0.675	0.389
1273	1	3734.9	23.620	9.136	0.925	1.121	0.640

\*Activating conditions:  $W_{ACT}/W_{COKE}=5$ , the rate of elevating temperature=10K/min,

$N_2$  flow rate=30ml/min T: activating temperature t: retaining time

D: average pore diameter  $D_{micro}$ : average micropore diameter

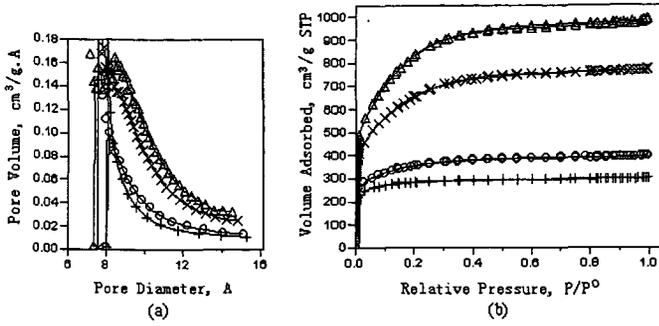
**Table 3.** Characterization of carbon molecular sieve structure

	$S_{BET}$ ( $m^2/g$ )	D ( $\text{\AA}$ )	$D_{micro}$ ( $\text{\AA}$ )	V (~20 $\text{\AA}$ ) $cm^3/g$	V(20-30 $\text{\AA}$ ) $cm^3/g$	V(30 $\text{\AA}$ -) $cm^3/g$
Untreated	2859.5	21.501	8.857	0.762	0.604	0.201
Preoxidation	2255.8	20.293	8.626	0.667	0.304	0.084

\*D: average pore diameter  $D_{micro}$ : average micropore diameter

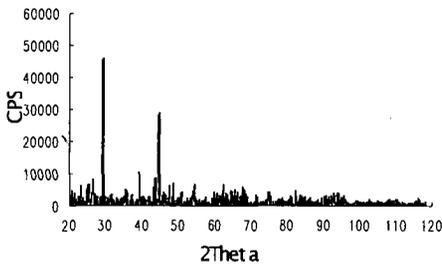
**Table 4.** Natural gas absorption capacity on carbon molecular sieves with different surface area

$S_{BET}$ ( $m^2/g$ )	V/V (3.0MPa)	V/V (4.0MPa)	V/V (5.0MPa)
1634	86.7	115.6	132.9
2069	127.1	144.2	156.7
2745	150.3	179.8	208.3



**Figure 1.** Characterization of carbon molecular sieve structure  
 (a): micropore distribution; (b): 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.** XRD patterns of carbon molecular sieve



(a) Derived from raw coke



(b) Derived from preoxidized coke

**Figure 3.** The SEM photo of carbon molecular sieves