THERMAL TREATMENT OF LIGNITE FOR CARBON MOLECULAR SIEVE PRODUCTION

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Abstract

Carbon molecular sieves (CMS) were prepared from Greek lignite by a thermal treatment technique involving three sequential stages: carbonization, followed by activation with an oxidizing agent, and aperture modification by coke deposition. Adsorption of N_2 at 77 K and CO_2 at 298 K was used for the characterization of products. Molecular sieving properties were examined by measuring the adsorption kinetic curves of CO_2 and CH_4 at room temperature. Activated samples with the highest surface area were selected for CMS production by employing a propylene cracking technique. High temperatures resulted in the production of materials with large differences in their BET and CO_2 surface areas. CO_2–CH_4 selectivity ratios estimated from the adsorption kinetic curves were high for these samples.

Keywords: carbon molecular sieves, coke deposition, propylene cracking, surface area

Introduction

Separation of gases, such as O_2 and N_2, by carbon molecular sieve (CMS) and pressure swing adsorption (PSA) has been constantly growing in comparison to other separation technologies such as cryogenic distillation or absorption [1]. In addition to air, other separations are now possible through the use of CMS, including carbon dioxide from methane, ethylene from ethane, hydrogen from refineries gases, and linear from branched hydrocarbons. A CMS contains a pore system formed of micropores with extensive adsorption volume and pore entrances of size equivalent to that of an adsorbing molecule [2]. Such proximity of pore walls at the pore entrance allows rapid diffusion of the smaller components of a gas mixture and slower diffusion of the larger components, resulting in the effective kinetic separation of the mixture. The ability to control the size of the pore openings or constrictions in a CMS to some Angstroms, is a major challenge in preparing CMS adsorbents. Since the adsorbent is the key component in the performance of the entire process, improved CMS adsorbents are needed to reduce the cost of gas mixture separations.

Generally CMS can be produced from carbonaceous precursors by using various treatment techniques which aim to tailoring pore apertures to match the size

of the desired adsorbate [3–5]. The pore structure of the initial precursor is initially fixed into a suitable pore range by a controlled thermal treatment which includes two sequential stages: carbonization carried out at 600–1000°C, followed by activation at 500–1000°C. This procedure results in the production of activated carbons with a wide pore size distribution (2–2000Å). The final pore size adjustment is usually accomplished by coke deposition at the pore openings from hydrocarbon cracking [6–8]. The properties of the produced CMS are quite variable and depend upon the carbonaceous precursors, the initial thermal treatment conditions and especially the final treatment procedure used for pore size tailoring. Proper selection of the precursor and adjustment of the manufacturing process conditions are considered necessary for the preparation of CMS with desirable pore dimensions for a specific separation.

The objectives of this work were to study the thermal treatment of a Greek lignite with a high mineral matter content for the production of carbon molecular sieves and to investigate the effect of experimental conditions on optimum pore structure development.

Experimental

The coal used in this study was a Greek lignite from the Ptolemais seam. The proximate analysis of this coal on a dry basis was 30.9 wt% ash, 52.8% volatile matter and 16.3% fixed carbon, while the ultimate analysis on a dry basis gave 36.2% C, 3.3% H, 1% N, 0.8% S and 27.8% O (by difference). The coal was ground and sieved and the 60–100 Tyler mesh fraction (particle size 150–250 μm) was subjected to thermal treatment.

CMS production commenced with the production of activated carbons by thermal treatment of lignite. Activation was carried out in a fixed bed reactor made of 1 1/2 inch diameter 316 SS tube, with a porous disc of Hastelloy plate (pore diameter 50 μm). The flow diagram of the reactor system is shown in Fig. 1. The reactor was heated to the desired temperature by a 5 kW electric furnace. Gas flow and temperature were controlled by the necessary instrumentation.

Activation temperatures used were 700, 800 and 900°C. The reactor was preheated to the desired temperature and purged with a continuous flow of 200 cm^3 min^{-1} N$_2$. About 2–3 g of coal were flashed into the reactor and pyrolysed for 1 h. The activation started when a mixture of N$_2$:CO$_2$=3:1 was introduced into the reactor. Char-coals were activated using different reaction times in order to prepare activated carbons with various burn-off levels. After a desired time elapsed, the reactor was rapidly cooled to room temperature while N$_2$ was passed through the reactor.

Carbon molecular sieves were prepared from activated carbon by coke deposition, derived from the thermal cracking of propylene. The heat treatment was carried out in a smaller diameter U-shaped fixed bed reactor made of an 1/2 inch 316 SS tube. Design of the activation reactor system permitted the use of the
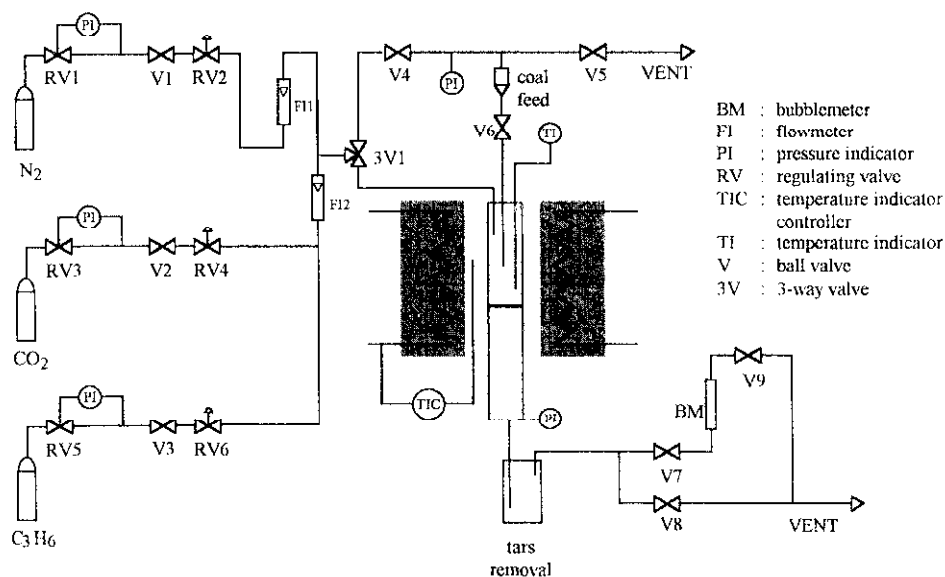
BM : bubblemeter
FI : flowmeter
PI : pressure indicator
RV : regulating valve
TIC : temperature indicator
controller
TI : temperature indicator
V : ball valve
3V : 3-way valve

Fig. 1 Flow diagram of the activated carbon unit

smaller reactor in the same unit. The reaction operating temperatures chosen were 500 and 700°C. The reactor was preheated to the desired temperature under a continuous nitrogen flow and 0.5 g of activated carbon were fed to the reactor. Coke deposition took place in flow of a gas mixture containing 10% v/v propylene in nitrogen. CMS with different coke deposition levels were prepared by using different reaction times.

Activated carbons and CMS were characterized by measuring the adsorption isotherms of N_2 at 77 K and of CO_2 at 298 K. A low temperature N_2 adsorption apparatus (Quantasorb, by Quantachrome) was used for the determination of N_2 adsorption isotherms. CO_2 adsorption data were obtained with a laboratory volumetric equipment. Surface areas were estimated from N_2 isotherms by using the BET multiple point equation and from CO_2 isotherms by using the Dubinin-Radushcevich equation. Prior to the measurement of N_2 adsorption, samples were outgassed at 383 K for 12 h under helium flow. For CO_2 adsorption measurements, samples were first oven dried at 383 K for 24 h, and then outgassed overnight at 383 K at a pressure of about 1 Pa.

Molecular sieving properties of produced CMS were evaluated by measuring the adsorption of CO_2 and CH_4 volumetrically under ambient conditions. Samples were degassed at 383 K under vacuum for 1 h prior to adsorption. Kinetic adsorption curves at 298 K were derived by calculating the amount of CO_2 or CH_4 adsorbed with time. The selectivity or uptake ratio, expressed as the ratio of the adsorbed amount of CO_2 to CH_4, at particular adsorption periods, was also determined.

Results and discussion

In this work CMS were prepared from activated carbons by employing a method of coke deposition. Before the coke deposition experiments, it was important to establish the behaviour of lignite during activation and to study the pore structure development of activated carbons. In this way, it will be possible to specify the appropriate activated carbon with the highest surface area which will be used as a starting material for CMS production.

Activated carbons were produced from the lignite by a two stage technique involving pyrolysis for the removal of volatile matter followed by activation with CO_2. The conversion of the overall reaction (carbonisation and activation), generally known as burn-off, is defined as the fraction of the reacted organic matter, according to the following equation:

$$Burn\text{-}off(\%) = [(W_{in}-W_{out}) / W_{in}] \times 100 \qquad (1)$$

where W_{in}, the initial mass of lignite on a dry, ash free basis; W_{out}, the final mass of sample on a dry, ash free basis.

In Fig. 2 the overal burn-off is shown as a function of activation reaction time and temperature. For chars activated at 900°C, the activation was complete after 45 min of activation. At lower temperatures, the reaction rate decreased, and for activation at 700°C, the burn-off was about 75% after 2.5 h of reaction. The high activation rate was attributed to the existence of a high inorganic matter content in the raw lignite. These inorganic components are known to be good catalysts for the gasification reactions of coals [9].

The adsorptive capacity of the activated carbons was studied by using N_2 as an adsorbate. Figure 3 shows typical N_2 adsorption isotherms for carbons activated at 800°C having different burn-off values. Since activated carbons are es-
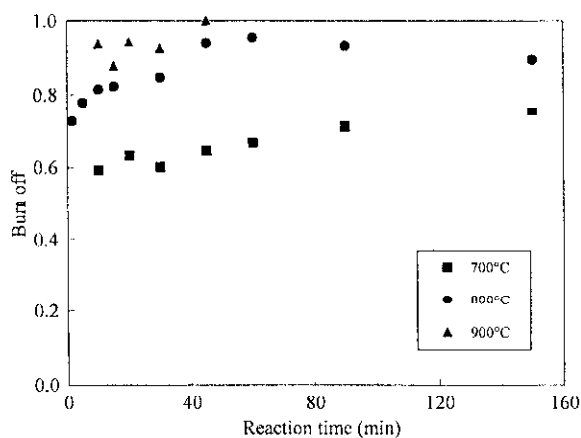

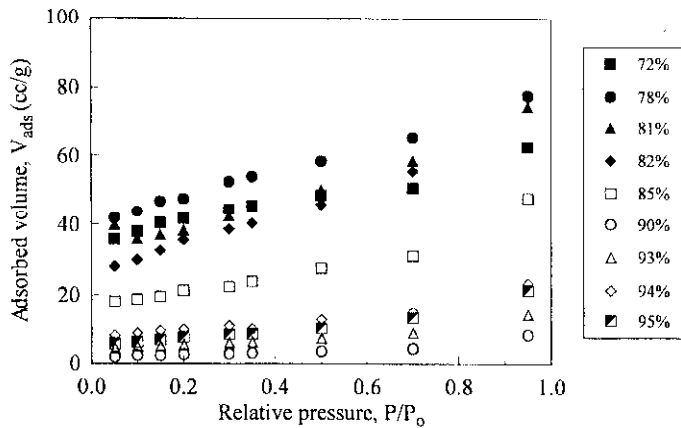Fig. 2 Activation burn-off of lignite as a function of time and temperature

Fig. 3 Nitrogen adsorption isotherms of lignite chars activated at 800°C

sentially microporous, the N_2 adsorption isotherms are of type I, having a very steep initial branch followed by a gradual approach to the linear branch at higher relative pressures.

The BET surface area of the prepared activated carbons is shown in Fig. 4 as a function of the overall burn-off, in the temperature range of 700–900°C. Surface area values are defined in m^2 per g of the total mass of the sample, including mineral matter. Surface area values range from 7 to 153 $m^2 g^{-1}$. As shown in this figure, the surface area increases up to a maximum value and then it declines. The initial increase is due to the opening of closed pores and the formation of new pores. The maximum surface area of 153 $m^2 g^{-1}$, was attained at a burn-off of about 78%, at 800°C. At longer activation times the surface area decrease indicates possible widening of micropores and/or coalescence of adjacent pores. At the highest temperature of 900°C, activation rate was high and resulted in activated carbons with high burn-off values and low surface areas.
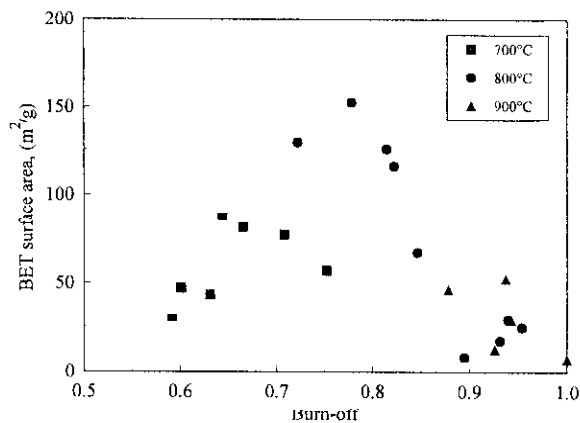

Fig. 4 BET surface area of activated carbons as a function of burn-off

In the case of microporous materials, surface areas estimated from N_2 adsorption, usually suffer from activated diffusion of N_2 at the low temperature of adsorption.

Therefore, adsorption of CO_2 at room temperature was also used for pore structure characterisation of the activated carbons. The CO_2 surface areas, estimated from the Dubinin-Radushkevich equation as a function of burn-off, are shown in Fig. 5. For samples activated at 700, 800 and 900°C, surface areas decrease with increasing activation and range between 20 and 205 m^2 g^{-1}. The highest surface area is reached by samples produced at 800°C, with a burn-off of about 80%.
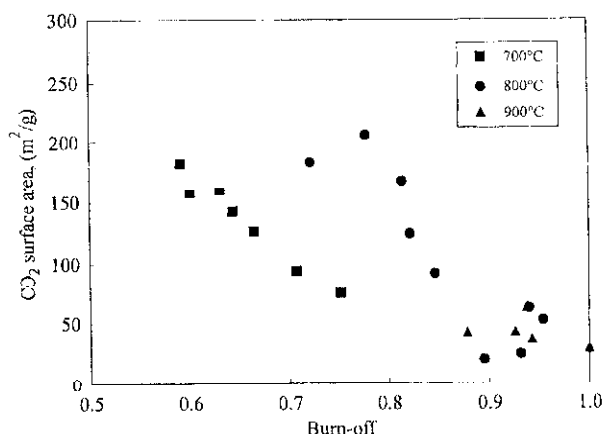

Fig. 5 CO_2 surface areas of activated carbons as a function of burn-off and temperature

The activated carbon which would be suitable for the production of carbon molecular sieves should present the following characteristics: (i) high surface area, in order to have high adsorptive capacity, and (ii) high percentage of micropores, for the preparation of pores with desired dimensions after coke deposition. In this study, the selection of the appropriate carbon has been based on two structural parameters: Micropore volume deduced from the application of the Dubinin-Radushkevich equation to the adsorption isotherms of N_2 at 77 K, V_o (N_2), and mesopore volume deduced from the adsorption isotherm of N_2 at 77 K, calculated by subtracting the value of V_o (N_2) from the amount adsorbed at P/P_o = 0.95, $V_{0.95}$ $(N_2) - V_o(N_2)$ [10].

The evolution of micropore and mesopore volume as a function of burn-off and activation temperature is shown in Fig. 6. In general, activation with carbon dioxide at low reaction times results in the production of exclusively microporous samples. Especially in the case of chars activated at 800°C, the proportion of mesoporosity is relatively small, below 20%, for burn-off values lower than 80%. However, intense activation conditions, such as high temperature (900°C) and extended reaction times, result in decrease of the micropores proportion in fa-
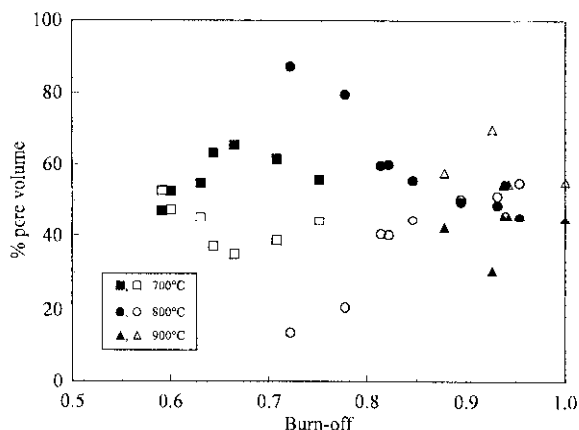
Fig. 6 Pore volume distribution of activated carbons as a function of burn-off (open symbols: mesopores; closed symbols: micropores)

vour of the development of mesopores. Activated carbons produced at 900°C, presented a mesopore volume proportion of over 55%. Taking into account the change of surface area with burn-off (Figs 4 and 5) it seems that carbon dioxide activation enhances the formation of new micropores at low burn-off values; at higher burn-off, above 80%, the widening of existing narrow micropores predominates, resulting in the production of mesoporous carbons.

These results suggest that the activated carbons with the most appropriate properties for the production of carbon molecular sieves are the samples with 70 to 78% burn-off, produced by CO_2 activation at 800°C. However the sample with the lower burn-off has a lower surface area ($129 \text{ m}^2 \text{ g}^{-1}$) than the activated carbon with 78% burn-off, which has the highest BET surface area of all samples ($153.5 \text{ m}^2 \text{ g}^{-1}$). Furthermore this sample has a high proportion of micropore volume (82%) in the total pore structure. This activated carbon was then used in the subsequent stage of propylene pyrolysis for carbon molecular sieve production.

Carbon deposition from pyrolysis of propylene was carried out on the selected microporous activated carbon with the highest surface area. This sample was exposed to a stream of 10% propylene in nitrogen at two temperatures. 500 and 700°C, for a period ranging from 5 to 60 min. Deposition results are depicted in Fig. 7, where the effect of reaction time on carbon loading is shown for the two temperatures. The effect of the gas phase propylene concentration on carbon deposition was investigated by exposing the activated carbon to two different concentrations of propylene, i.e. 10% and 20% propylene in N_2 at 500°C.

At low propylene concentration and temperature, the deposition rate is slow. About 5% carbon loading is achieved after 1 h of reaction. The deposition increases with temperature, although at 700°C a small carbon loading is observed during the first 20 min of reaction, compared to 500°C. However, upon further pyrolysis, a sharp increase in carbon deposition takes place, resulting in about
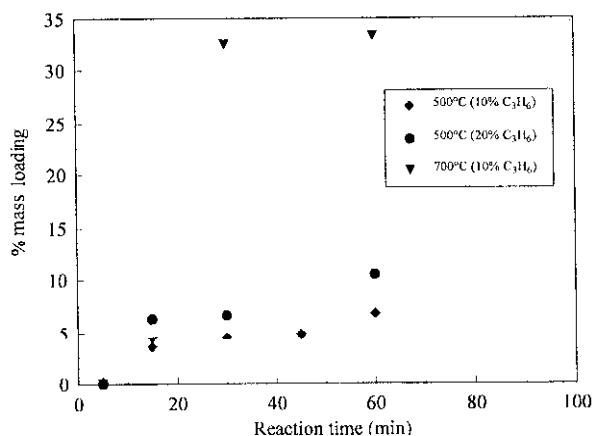
Fig. 7 % mass loading produced by coke deposition from propylene cracking on activated carbon as a function of time and temperature

33% loading after 30 min of exposure. Finally, a small increase in the mass loading to a value of 34% is observed after 1 h of reaction suggesting that carbon deposition from the propylene cracking essentially stops at extended reaction times, possibly due to the closure of pores accessible to propylene [7,11]. Mass loading increases with propylene concentration in the gas stream. After 1 h of activated carbon exposure in a stream of 20% propylene at 500°C, carbon deposition was about 10%.

Results indicate that the rate and amount of propylene cracking over the microporous activated carbon depends upon cracking conditions such as temperature, time and propylene partial pressure. Intense pyrolysis conditions, such as high temperature and propylene concentration favour carbon deposition, while at mild conditions of low temperatures and concentration, low rates of deposition are achieved.

The pore structure of CMS was again evaluated by N_2 and CO_2 adsorption. The BET surface area values of the samples are shown in Fig. 8 as a function of reaction time and temperature. For all samples, surface area decreases with reaction time. For samples prepared at 500°C and 10% C_3H_8, surface areas vary between 80–120 m^2 g^{-1}. The highest value was obtained after 2 min of reaction. At 500°C and 20% propylene, surface areas are lower that at 10% C_3H_8. Areas decline even faster at elevated temperatures (700°C), even at low C_3H_8 concentrations, down to about 25 m^2 g^{-1}.

Surface areas estimated from CO_2 adsorption at 298 K are shown in Fig. 9 as a function of reaction time and temperature. At low temperature of 500°C, the deposition of 10% propylene results in samples with areas between 130 to 180 m^2 g^{-1}. The sample prepared at the highest reaction time of 3 h gives the highest area, while the areas of the remaining samples vary between 130 and
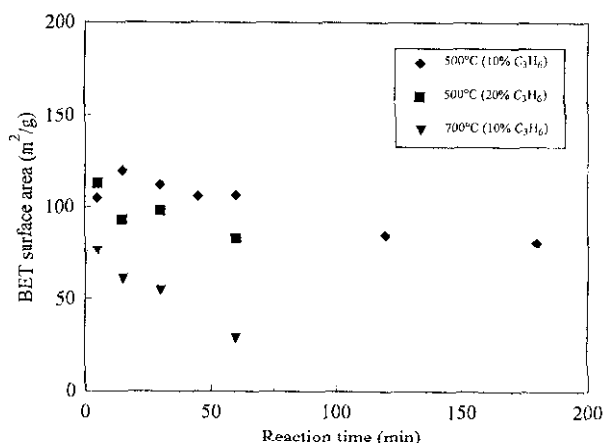
Fig. 8 BET surface area of CMS as a function of time, temperature and propylene concentration

$165 \ m^2 \ g^{-1}$. Similar values, $135-167 \ m^2 \ g^{-1}$, are obtained for samples produced at the same temperature ($500^\circ C$) under a flow of 20% propylene. However, lower areas (104 to $164 \ m^2 \ g^{-1}$) were obtained with propylene pyrolysis at $700^\circ C$. As shown in Fig. 9, CO_2 surface areas change little with reaction time, but they decrease with temperature.
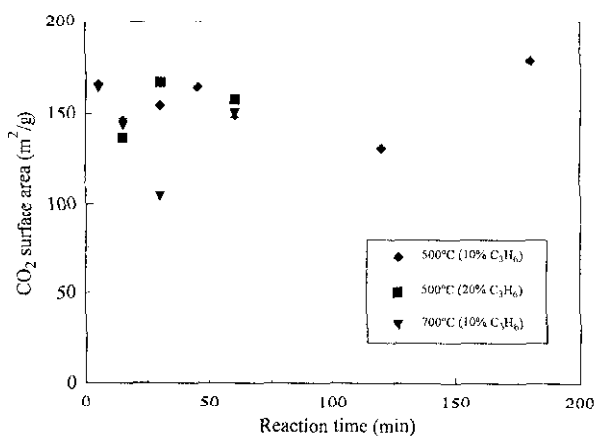

Fig. 9 CO_2 surface areas of propylene cracked samples as a function of reaction time and temperature

Kinetic adsorption curves of CO_2 and CH_4 were used to estimate the molecular sieving behaviour of samples for the separation of gases. Figure 10 shows the adsorption curves for samples prepared by cracking of propylene at various concentrations and at 500 and $700^\circ C$. Table 1 gives the selectivity ratio of CO_2-CH_4 estimated from the adsorption kinetic curves at 10 min. This time was selected,
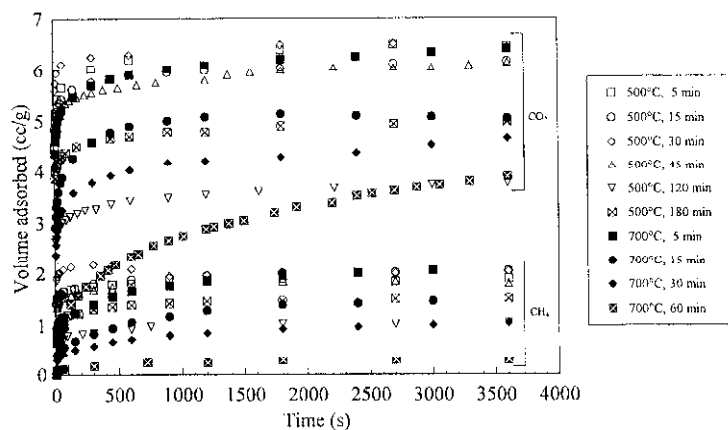
Fig. 10 Kinetic adsorption curves of CO_2 and CH_4 on CMS

Table 1 Selectivity ratios of activated carbons after propylene cracking, estimated from kinetic adsorption curves at 10 min

Temperature/°C	Cracking time/min	% Propylene	Selectivity ratio
500	5	10	3.5
500	15	10	3.2
500	30	10	3.1
500	45	10	3.3
500	120	10	3.7
500	180	10	3.4
500	5	20	3.5
500	15	20	3.6
500	30	20	3.1
500	60	20	2.9
700	5	10	3.6
700	15	10	4.7
700	30	10	5.4
700	60	10	8.6

as the adsorption of both gases has almost attained in equilibrium conditions after 10 min. From this figure it is apparent that CO_2 uptake is in all cases higher than that of CH_4. For samples prepared at 500°C, the uptake curves are quite similar and decrease at long cracking times of 2 and 3 h. Selectivity ratios at 10 min vary between 3.1 and 3.7. A significant reduction in uptake capacity is observed for samples prepared at 700°C especially at long reaction periods. For

these samples, CO_2 uptake at 10 min is decreasing with cracking time from 5.9 to 2.3 ml g^{-1}. Higher reductions in equilibrium uptake, from 1.64 to 0.27 ml g^{-1}, are observed for CH_4. The selectivity ratios of samples prepared at 700°C, estimated from the uptake curves at 10 min, vary between 3.6 to 8.6 and they are higher than the ones of samples prepared at 500°C. An almost two-fold increase in the CO_2–CH_4 uptake ratio is observed for samples prepared at high temperature and long reaction times compared to samples prepared at low temperature. Similar CO_2–CH_4 selectivity ratios (of about 9) estimated from adsorption kinetic curves at 10 min, have been reported for CMS produced from bituminous coals by acetylene and benzene cracking [6].

From these results it is apparent that hydrocarbon cracking under harsh experimental conditions favours extended coke deposition, thus resulting in the closure of mesopores and in sharp decrease of BET surface area values with reaction time. However, at high temperatures, reaction rate appears to be faster than diffusion and propylene cracking takes place mainly at the particle surface. Thus, the micropores and the CO_2 surface area are not affected, resulting in samples with molecular sieving properties. Under mild conditions, hydrocarbon cracking gives more uniform and controllable coke deposition on the internal pore structure, resulting in samples with comparable BET and CO_2 areas. Apparently, reaction and diffusion rates are comparable at low temperatures, and propylene molecules penetrate deeper into the pores. As a result, coke is deposited on the pore walls, leading to samples with almost equal BET and CO_2 surface areas, which have low selectivity ratios. Thus, selection of proper experimental conditions is important for successful conversion of microporous carbons to useful molecular sieves.

It should be mentioned that the raw lignite used here for the production of CMS, has a high mineral matter content which can affect not only the kinetics of activation and propylene cracking reactions [12], but it can also alter the pore structure development [13]. Removal of inorganic matter by acid washing of lignite results exclusively in porous materials with high BET and CO_2 surface areas, which could be suitable as precursors for CMS production.

Conclusions

Carbon molecular sieves were produced from Greek lignite with a high mineral matter content by a thermal treatment technique involving three successive stages: carbonisation, followed by activation with CO_2, and finally pore aperture modification by coke deposition. Rapid activation rates observed at high temperatures, were attributed to the catalytic action of inorganic matter in the lignite ash. Activated samples with the highest surface area were selected for CMS production by employing propylene cracking as a coke depositing reaction. The rate of coke deposition increased with the temperature, reaction time and propylene concentration in the feed gas mixture. These factors also affected the pore struc-

ture development. Extended coke deposition was obtained at high temperature, resulting in closure of the mesopores, and in sharp decrease of BET surface area without affecting the micropore surface area. Kinetic adsorption curves of CO_2 and CH_4 on samples prepared by propylene cracking, gave high selectivity ratio values comparable to those achieved with CMS from bituminous coals. Mild experimental conditions of low temperature and low propylene concentration gave a more uniform coke deposition on the micropore walls and resulted in samples with low CO_2–CH_4 selectivities.

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References

1 M. Srivastava and H. Singh, Erdöl und Kohle-Erdgass-Petrochemie Vereinigt mit Brennstoff Chemie, 47 (1994) 242.
2 H. Jüntgen, K. Knoblauch and K. Harder, Fuel, 60 (1981) 817.
3 A. L. Cabrera, J. E. Zehner, C. G. Coe, T. R. Gaffney, T. S. Farris and J. N. Armor, Carbon, 31 (1993) 969.
4 R. K. Mariwala and H. C. Foley, Ind. Eng. Chem. Res., 33 (1994) 607.
5. S. N. Vyas, S. R. Patwardhan, C. Vijayalakshmi and B. Gangadhar, Fuel, 72 (1993) 551.
6 S. N. Vyas, S. R. Patwardhan and B. Gangadhar, Carbon, 30 (1992) 605.
7 S. K. Verna and P. L. Walker Jr., Carbon, 30 (1992) 829.
8 S. K. Verna and P. L. Walker Jr., Carbon, 31 (1992) 1203.
9 P. Samaras, E. Diamadopoulos and G. P. Sakellaropoulos, Carbon, 32 (1994) 771.
10 F. Rodriguez-Reinoso, M. Molina-Sabio and T. M. Gonzalez, Carbon, 33 (1995) 15.
11 J. Garrido, A. Linares-Solano, M. Martin-Martinez, M. Molina-Sabio, F. Rodriguez-Reinoso and R. Torregrosa, Langmuir, 3 (1987) 76.
12 M. Kamishita, O. P. Mahajan and P. L. Walker Jr., Fuel, 56 (1977) 444.
13 P. Samaras, E. Diamadopoulos and G. P. Sakellaropoulos, Carbon, 29 (1991) 1181.