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CO_2/CH_4 AND O_2/N_2 KINETIC SELECTIVITIES OF OIL PALM SHELL-BASED CARBON MOLECULAR SIEVES

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ABSTRACT

Carbon molecular sieves (CMS) have become an interesting area of adsorption due to their microporous nature and favourable separation factor on size and shape selectivity basis for many gaseous systems. In this work, CMS were prepared from locally available oil palm shell by thermal treatment of carbonization followed by steam activation, then benzene deposition. The carbonization of dried palm shell at 900°C for 1 hr followed by steam activation at 30-420 min produced activated carbons with various degrees of burn-off. The highest micropore surface area and micropore volume of the activated samples were obtained at 53.2% burn-off. This sample was found suitable to be used as precursor for CMSs production in the deposition step. Subsequent benzene deposition onto activated samples at temperatures from 600°C-900°C for various benzene concentrations resulted in a series of CMS with different O_2/N_2 and CO_2/CH_4 kinetic selectivities.

Keywords: palm shell, activation, benzene deposition, carbon molecular sieves.

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INTRODUCTION

Oil palm is the main agricultural crop in Malaysia with a total planted area of 3.9 million hectares and oil production of 15.9 million tonnes in 2006 (Abdullah and Lazim, 2006). The total area is expected to increase further due to the rapid expansion of the oil palm industry. In production of palm oil, about 4.6 million tonnes of shell are produced as a by-product annually (Ngan, 2002). Currently, the shell is largely wasted with only some burnt as fuel to produce steam in the oil palm mill (Harimi *et al.,* 2005). One such way to enhance its value is to produce CMS. CMS are activated carbons with homogeneous pores of several angstroms in diameter (Casa-Lillo *et al.,* 1998). This pore characteristic confesses it a selective adsorption property. Currently, CMS is used to remove nitrogen from air by pressure swing adsorption (PSA). The O_2 is separated from N_2 by allowing the smaller O_2 molecules to fill the carbon micropores before the N_2.

CMS are produced from a variety of carbonaceous materials such as coconut shell (Vyas *et al.,* 1994; Kim *et al.,* 2002), walnut shell (Zhonghua and Vansant, 1995; David *et al.,* 2004), various nut shells (Nguyen and Do, 1995), lignite (Samaras *et al.,* 1998) and anthracite (Lozano-Castello *et al.,* 2005). There are basically two approaches to produce CMS; controlled pyrolysis of the carbon precursor and modification of the existing porosity of an activated structure through carbon deposition (Miura, 1999). In controlled pyrolysis, the precursor is pyrolyzed at a suitable temperature and under specific conditions. The adsorption capacity is increased by creation of micropores without excessive widening of the pores, which can be detrimental to selectivity. CMS produced by this method has a low adsorption capacity (Tan and Ani, 2004). CMS prepared by modifying the existing porosity of an activated structure through carbon deposition is preferred, being a better product with higher adsorption and selectivity (Villar-Rodil *et al.*, 2005; Vyas *et al*., 1994; Zhonghua and Vansant, 1995; Nguyen and Do, 1995; Cabrera *et al.,* 1993). The high adsorption is conferred by the high micropore surface area and selectivity

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by the carbon deposited (Villar-Rodil *et al.*, 2002). According to Samaras (1998), the activated carbon with which to produce the CMS should posses: (i) a high percentage of micropores, and (ii) high micropore volume, in order to have high adsorption.

If CMS are made directly from a raw material, the carbonization and activation steps must be carefully controlled to obtain an activated carbon with high micropore surface area before deposition is done. Otherwise the deposition will be on the walls of the mesopores, closing off the micropore (Kawabuchi *et al.*, 1998). In this work, palm shell-based activated carbon was prepared first by carbonization, followed by steam activation before being subjected to deposition. The CMS performances were assessed by its O_2/N_2 and CO_2/CH_4 kinetic selectivities.

EXPERIMENTAL WORK

Materials

The major material used in this study was palm shell of *tenera* fruit type, obtained from a local oil palm mill. The gases used were supplied by Nippon Oxygen Sdn Bhd with the following purities: methane (99.995%), nitrogen (99.999%), oxygen (99.999%) and carbon dioxide (99.995%). The hydrocarbon used as carbon source for deposition was benzene (Merck, analytical grade).

Procedures

Activated carbon from the palm shell was prepared by conventional carbonization followed by steam activation. Steam activation was used because it produces activated carbons with larger micropore volumes (Jasieńko-Halat and Kedzior, 2005). The carbonization and activation apparatus and the preparation procedure are described elsewhere (Wan Daud and Wan Ali, 2004). The shell was grounded and sieved to 1.0 to 2.0 mm. Then, 500 g of shell was carbonized at 900°C for 1 hr under nitrogen flow before being activated with steam for 30-420 min to achieve a burn-off of 0%-60%. After the desired time lapse, the reactor was cooled to room temperature under nitrogen flow. The different activated carbons were indicated by the degree of carbon burn-off, θ (wt%) achieved, which was calculated as follows:

$$\theta = \frac{W_I - W_T}{W_I} \times 100 \qquad (1)$$

where W_I is the initial mass of the sample before activation, and W_T the mass of the sample after activation. Carbon deposition was carried out in a stainless steel reactor (6.9 cm diameter and 100 cm length) equipped with a vertical tubular furnace and pre-heater. The deposition temperatures used varied from 600°C to 900°C, with the most suitable temperature then used for the benzene concentration study. The deposition time and nitrogen flow rate were fixed at 30 min and 20 ml s^{-1}, respectively. After the benzene deposition, the reactor was purged with nitrogen to cool it down to room temperature.

Characterization

All the samples were characterized by N_2 (77K) adsorption in a Micromeritics ASAP 2010 volumetric adsorption apparatus. The surface area was derived from the adsorption isotherms using the Brunauer-Emmett-Teller (BET) equation, and the Dubinin-Radushkevich (DR) equation used to calculate the micropore volume over a range of relative pressure of 1.1×10^{-5} to 0.02. The total volume (V_t) was obtained at a relative pressure of 0.99 (Zhang *et al.*, 2005). Prior to measurement, the samples were degassed at 120°C for 12 hr in the degas pot of the adsorption analyser. For the kinetic study, the CMS samples prepared were allowed to adsorb various gases such as O_2, N_2, CO_2 and CH_4 at 25°C. Kinetic adsorption data was obtained using an adsorption rate software in the same apparatus as in the characterization analysis. After degassing, a known volume of gas at 360 mmHg was introduced into the system and the decrease in pressure monitored at 0.2 s intervals for the first 30 s, and then at 1 s intervals thereafter.

RESULTS AND DISCUSSION

Characterization of Activated Samples

Table 1 lists the burn-offs of six activated carbon samples. The percentage burn-offs increased with the time of activation. This is attributed to the reaction occurring inside the particles, which created the necessary internal pore structure. A similar trend was observed by Daguerre *et al.* (2000) for activated carbon produced from petroleum pitch. Prolonged activation allowed the steam to increase the porosity of the activated sample.

The effects of activation time on the surface area and pore volume of the activated carbon are shown in *Figures 1* and *2*, respectively. The BET surface area

TABLE 1. BURN-OFFS OF ACTIVATED CARBONS

Sample	t_{act} (min)	Burn-off (%)
AC30	30	16.1
AC90	90	31.3
AC160	160	45.1
AC250	250	53.2
AC340	340	57.2
AC420	420	58.7

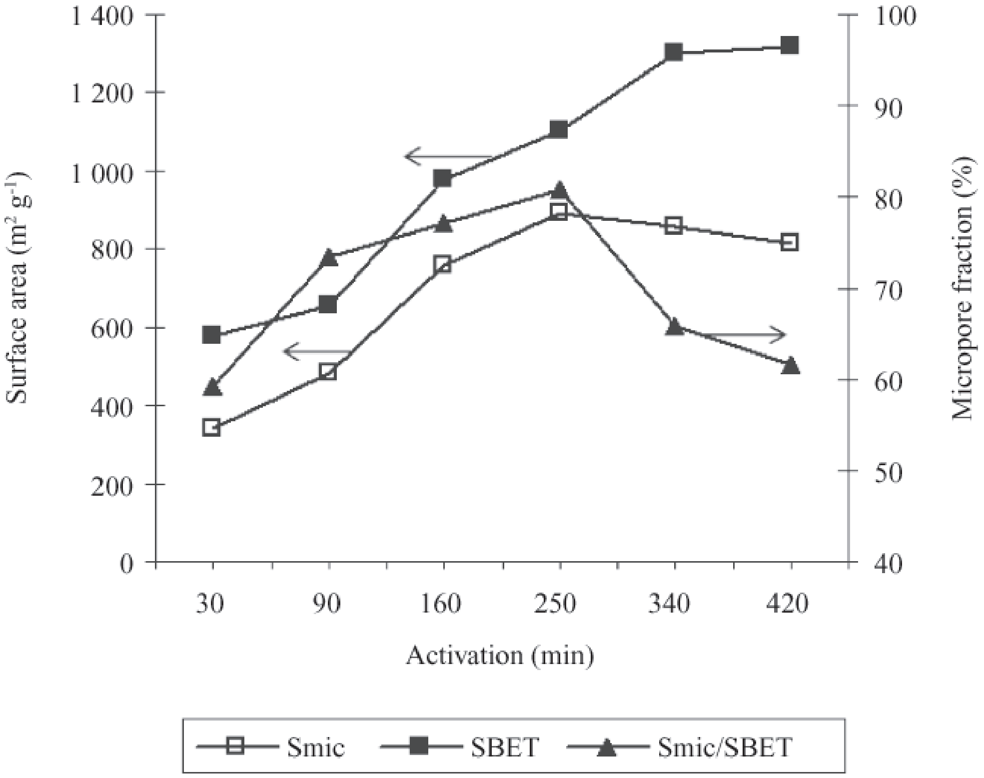

Figure 1. Effect of activation time on the surface area of the activated carbon.

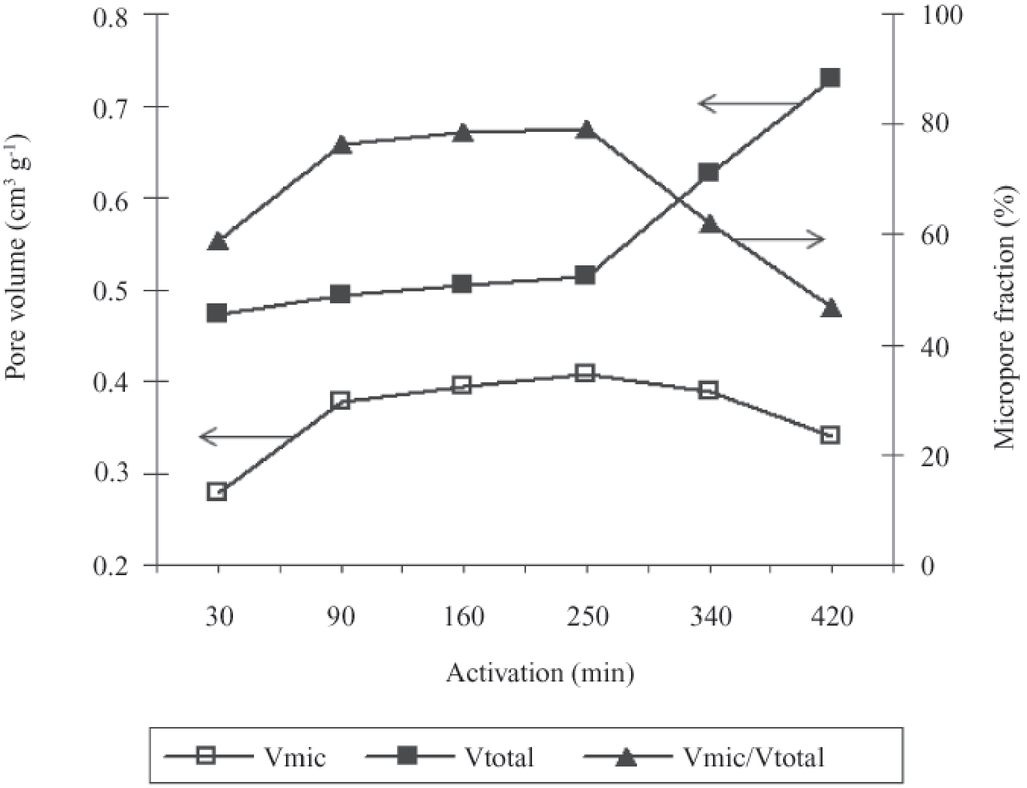

Figure 2. Effect of activation time on the total pore volume of the activated carbon.

(S_{BET}) and total volume (V_{total}) increased with the activation time to a maximum at 420 min. This is attributed to the diffusion of water molecules into the interior, developing a larger pore network (Wigmans, 1989). The micropore surface area (S_{mic}) and micropore volume (V_{mic}) were maximal at an activation time of 250 min, indicating the continuous development of microporosity with creation of new pores. The deposit of tarry material was cleared and the carbon exposed to the activation agent. However beyond time, both values decreased as the micropores began to widen into mesopores (Hazeleger and Martinez, 1992; Gergova *et al.*, 1993; Samaras *et al.*, 1998).

Figure 3 shows the adsorption isotherm of activated carbon with different degrees of burn-off. For all the activated samples, except AC340 and AC420, the plateau indicated that they are Type I, or microporous, materials. Meanwhile the isotherms of AC340 and AC420 indicated some mesoporosity development in addition to their microporous nature. These results showed that the AC250, which had the highest microporosity, is suitable for use as precursor for CMS production.

Effect of Benzene Deposition Temperature

TABLE 2. CARBON MOLECULAR SIEVES (CMS) PROPERTIES WITH VARIOUS DEPOSITION TEMPERATURES

CMS sample	**T_{dep} (°C)**	**W_{gain} (mg g^{-1})**	**S_{BET} (m^2 g^{-1})**	**V_{mic} (cm^3 g^{-1})**
C600	600	38.4	932	0.381
C700	700	39.2	847	0.394
C800	800	41.3	704	0.412
C900	900	43.5	621	0.294

Characterization of CMS. *Table 2* shows the properties of CMS produced with respect to deposition temperatures. The CMS micropore volume increased with deposition temperature up to 800°C, beyond which a large drop occurred to 900°C. The phenomenon suggests that at low temperature, the deposition occurs on the entire pore walls, resulting in low micropore volume. At moderate temperature, the micropore volume increased with carbon deposition at the pore mouth without diffusing inside to the pore wall. In addition, some of the large pores narrow down to micropores. At high temperature, benzene may be pyrolyzed in the gaseous phase and the carbon deposited on the exterior surface of the particles, closing off some of the pores (Kawabuchi *et al.*, 1996; Freitas and Figueiredo, 2001).

Adsorption Kinetics of CMS

To assess the suitability of an adsorbent for the desired separations, it is useful to plot the variation in uptake of gases with time. *Figure 4* shows the uptake curves of O_2 and N_2, and *Figure 5* the uptake curves of CO_2 and CH_4 by CMS produced at different deposition temperatures. All the CMS samples adsorbed all the gases very rapidly within 10 s. The sorption rates for the gases were in the

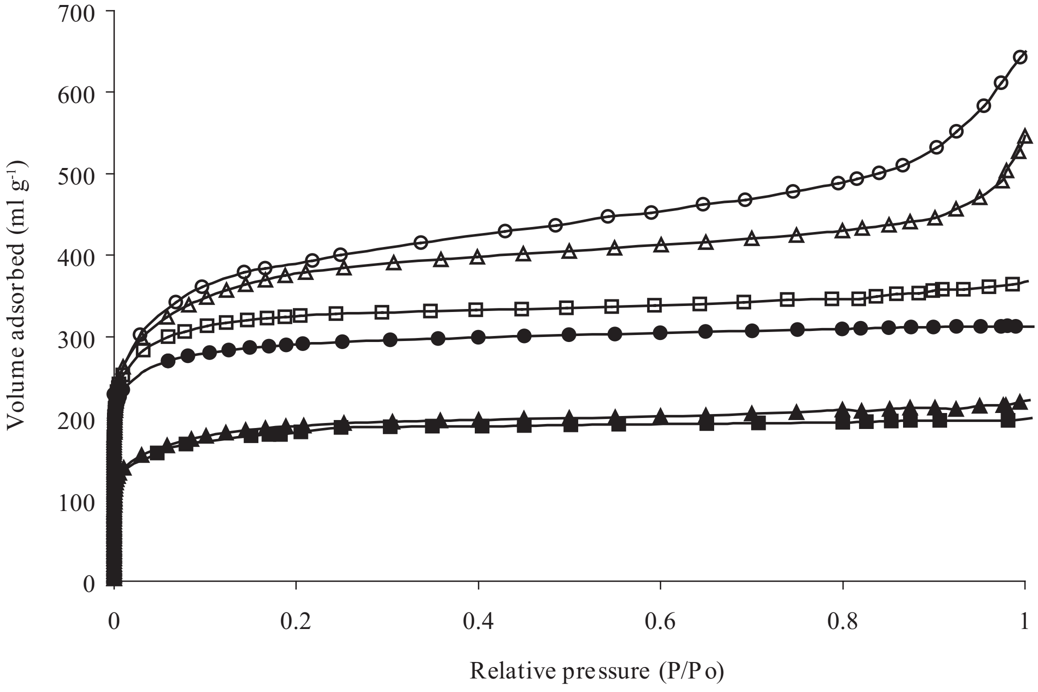

Figure 3. Adsorption isotherms of activated carbon with different degrees of burn-off; 16.1% (■), 31.3% (▲), 45.1% (●), 53.2% (□), 57.2% (g) and 58.7% (p).

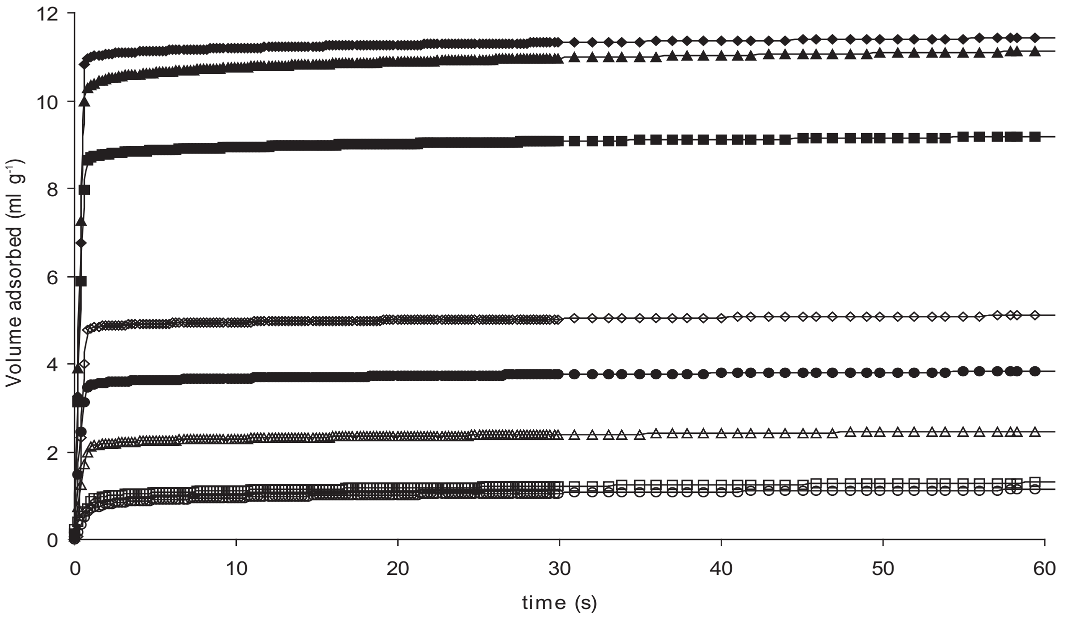

Figure 4. Adsorption kinetics of O_2 and N_2 at 25°C; (filled symbols: O_2; open symbols: N_2); C600 (◆), C700 (▲), C800 (■) and C900 (●).

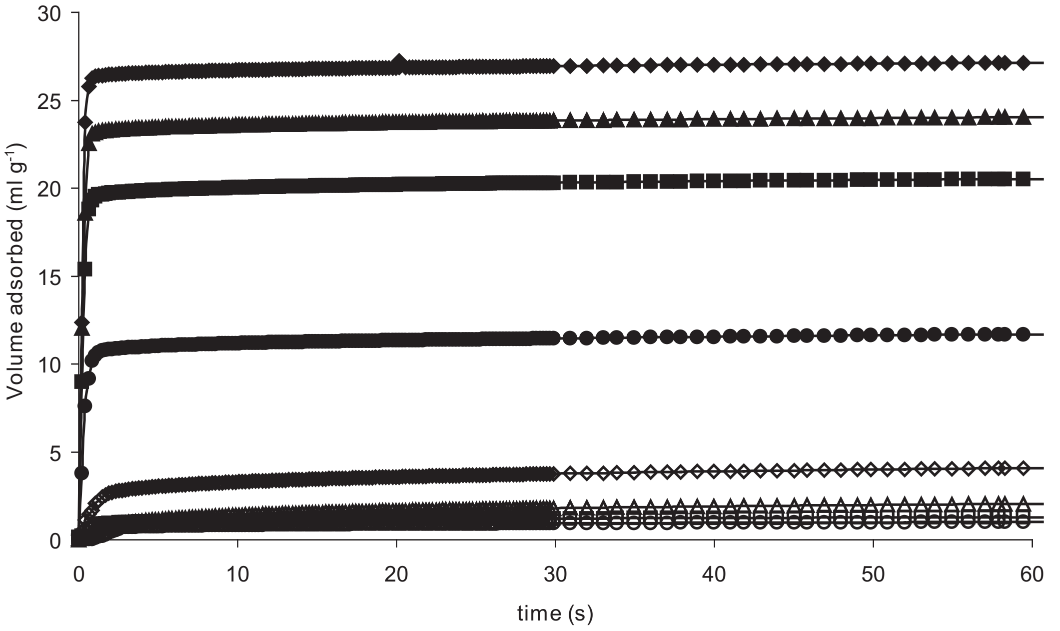

Figure 5. Adsorption kinetics of CO_2 and CH_4 at 25°C; (filled symbols: CO_2; open symbols: CH_4); C600 (◆), C700 (▲), C800 (■) and C900 (●).

order: $CO_2 > O_2 > N_2 > CH_4$, in agreement with earlier studies by Vyas *et al.* (1994), Kim *et al.* (2002) and De Salazar *et al.* (2005). Up to 800°C deposition temperature, the N_2 (molecular diameter 0.36 nm) and CH_4 (0.38 nm) adsorptions were much lower than those for O_2 (0.34 nm) and CO_2 (0.33 nm). At 900°C deposition temperature, there was a decrease in adsorption for all gases, which reduced the O_2/N_2 and CO_2/CH_4 selectivities.

Table 3 gives a better picture of the kinetics of adsorption for the gas pairs by the CMS samples. Almost three-fold increases in both O_2/N_2 and $CO_2/$

TABLE 3. GAS UPTAKE AND SELECTIVITIES AT 60 s

CMS sample	Uptake value (cm^3 g^{-1}) at 60 s				S_{60}	
	O_2	N_2	CO_2	CH_4	O_2/N_2	CO_2/CH_4
C600	11.42	5.10	27.13	4.07	2.24	6.66
C700	11.12	2.46	24.03	2.04	4.52	11.80
C800	9.17	1.30	20.52	1.28	7.06	16.00
C900	3.82	1.13	11.69	1.01	3.39	11.55

Notes: Adsorption pressure: 360 mm Hg.
Adsorption temperature: 25°C.

CH_4 selectivities was observed by the CMS sample prepared at 800°C compared to the sample prepared at 600°C. Beyond that, there was no further improvement in the selectivities. A similar trend in kinetic selectivities has been reported for CMS produced from coconut shell by Kim *et al.* (2002). From these results, the deposition temperature of 800°C was chosen to further study the effect of benzene concentration on the CMS properties and selectivity.

Effect of Benzene Concentration

Characterization of CMS. *Table 4* shows the properties of CMS produced in nitrogen flow with different benzene concentrations. By increasing the benzene concentration, the weight gain and micropore volume were almost constant. However, the surface area decreased with higher benzene concentration. It is clear that the effect of benzene concentrations in the range studied had less effect on the CMS properties than the deposition temperature.

Adsorption Kinetics of CMS

Figure 6 shows the uptake curves of O_2 and N_2 and *Figure 7* the uptake curves of CO_2 and CH_4 by CMS produced at different benzene concentrations. All the CMS samples had only small adsorption rates for N_2 and CH_4, indicating their excellent selectivity for separating O_2/N_2 and CO_2/CH_4. The small adsorption of N_2 and CH_4 compared to those for O_2 and CO_2 was caused by the molecular sizes of N_2 and CH_4 being close to the average micropore size of the CMS. As the benzene concentration increased until 30 vol.%, there were only small increases in the O_2/N_2 and CO_2/CH_4 selectivities. Beyond that, there was no further improvement in the both selectivities. *Table 5* shows the kinetics for the two gas pairs by the CMS samples. It appears that the benzene concentration had less effect on the kinetic selectivity than the deposition temperature. The O_2/N_2 and CO_2/CH_4 selectivities were only slightly increased up to 30 vol.% benzene concentration, after which, no further improvement occurred.

TABLE 4. CARBON MOLECULAR SIEVES (CMS) PROPERTIES

CMS sample	% vol. C_6H_6 in N_2	W_{gain} (mg g^{-1})	S_{BET} (m^2 g^{-1})	V_{mic} (cm^3 g^{-1})
C800/10	10	38.4	752	0.408
C800/20	20	40.8	734	0.410
C800/30	30	41.3	704	0.412
C800/40	40	41.5	681	0.412

TABLE 5. GAS UPTAKE AND SELECTIVITIES AT 60 s

CMS sample	Uptake value (cm^3 g^{-1}) at 60 s				S_{60}	
	O_2	N_2	CO_2	CH_4	O_2/N_2	CO_2/CH_4
C800/10	10.32	1.62	22.73	1.51	6.37	15.03
C800/20	9.75	1.44	21.32	1.38	6.77	15.42
C800/30	9.17	1.30	20.52	1.28	7.06	16.00
C800/40	8.84	1.26	19.36	1.21	7.02	16.00

Notes: Adsorption pressure: 360 mm Hg.
Adsorption temperature: 25°C.

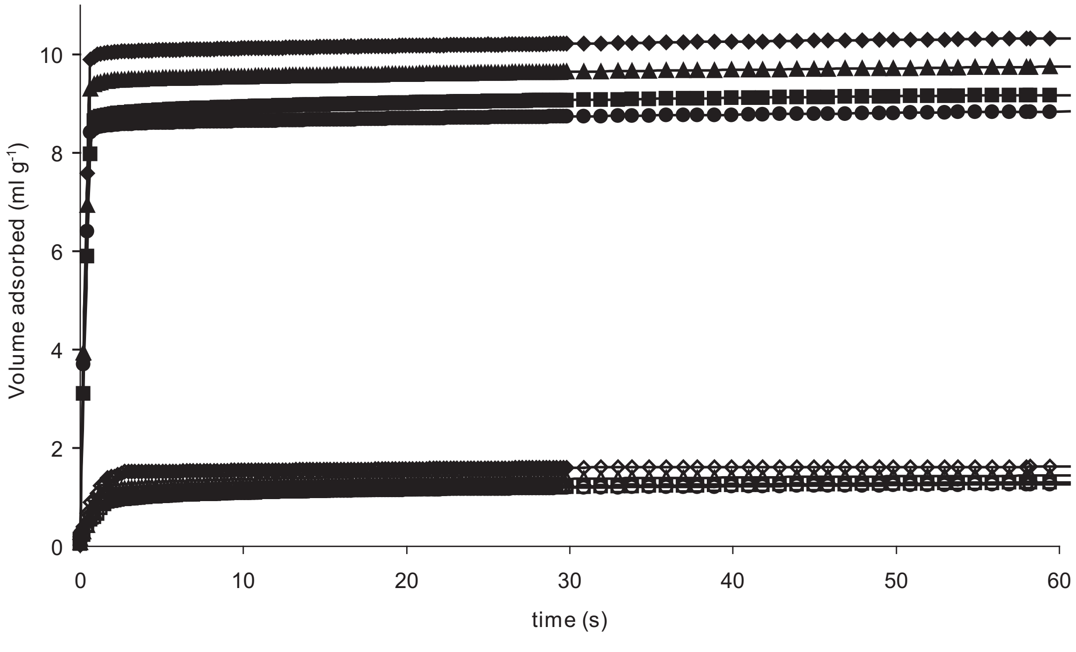

Figure 6. Adsorption kinetics of O_2 and N_2 at 25°C; (filled symbols: O_2; open symbols: N_2); C800/10 (◆), C800/20 (▲), C800/30 (■) and C800/40 (●).

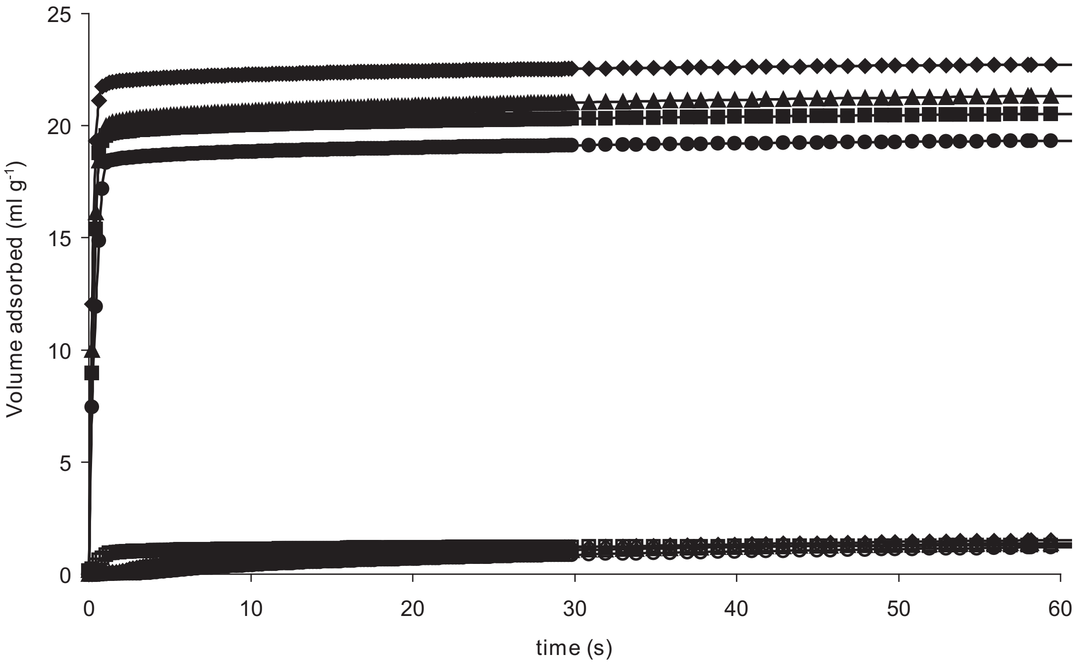

Figure 7. Adsorption kinetics of CO_2 and CH_4 at 25°C; (filled symbols: CO_2; open symbols: CH_4); C800/10 (◆), C800/20 (▲), C800/30 (■) and C800/40 (●).

CONCLUSION

Palm shell was used to prepare CMS by carbonization, followed by activation and carbon deposition. The carbonized palm shell, activated by steam for 250 min gave the highest micropore volume of 0.4067 cm^3 g^{-1}. The kinetic selectivity in CMS were found to depend greatly on the deposition temperature. There were almost three-fold increases in both the O_2/N_2 (7.06) and CO_2/CH_4 (16.0) kinetic selectivities by the CMS samples prepared at 800°C over those the sample prepared at 600°C. There was not much effect from the benzene concentration on the selectivities compared to the effect by the deposition temperature.

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