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Preparation of carbon molecular sieves from palm shell: effect of benzene deposition conditions

M.A. Ahmad

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Abstract Application of carbon molecular sieve (CMS) for gas separation has been found much attention recently. In this work, CMS was prepared from locally available palm shell through carbonization, steam activation and carbon vapour deposition (CVD) technique. After carbonization step, the char produced was subjected to steam activation at various activation times. The activated carbon obtained at 53.2% burn-off, which contain the highest amount of micropore volume was further used in CVD step by using benzene vapour at various deposition conditions. The performance of CMSs produced was examined by assessing the adsorption kinetics of O_2, N_2, CO_2 and CH_4 gases. All CMS samples showed a small N_2 and CH_4 uptake compared to the O_2 and CO_2. The suitable conditions for CVD were found at 800°C, 30 min and 30 vol% benzene of deposition temperature, time and benzene concentration, respectively. At this point the O_2/N_2 and CO_2/CH_4 uptake ratios arrived 7.1 and 16.0, respectively.

Keywords Adsorption · Palm shell · Carbon molecular sieves · Uptake ratio

1 Introduction

Gas separations are a major production cost in the chemical industry today. Production of industrial gases by pressure swing adsorption (PSA) is expected to grow much faster than by the cryogenic distillation. PSA utilizes CMS as adsorbent to separate various gases, especially nitrogen from air (Ruthven 1984). CMS is a microporous material having a pore size similar to that of the critical dimensions of the gas molecules to be separated (Reid and Thomas 2001). The pore surface area of CMS is usually less, and the pore size distribution narrower than that of commercial activated carbons.

Several methods have been developed for CMS production such as pyrolysis (Braymer et al. 1994), activation and carbon vapour deposition (CVD) (Vyas et al. 1994; Nguyen and Do 1995; Villar-Rodil et al. 2005; Freitas and Figueiredo 2001; Kawabuchi et al. 1996). Among them, the CVD approach has been found particularly suitable and has received considerable attention. By this approach, an active carbon of high adsorption capacity is conferred molecular selectivity through CVD at the micropore mouths, thus reduced the pore size. Properly prepared CMS required that the sizes of carbon species entering the micropores be limited so that the overall adsorptive capacity of the material is as high as possible (Hu and Vansant 1995). The carbon species should have adequate reactivity to be adsorbed and pyrolyzed on the pore mouth. It must also have an appropriate shape to produce a flat coating on the pore mouth. In addition, the hydrocarbon should have high chemical stability in the gas phase and not produce intermediate species, which make deposition easier to be controlled (Kawabuchi et al. 1996). Thus the pore mouth will narrow to the smallest dimension of the hydrocarbon molecule.

Accordingly, benzene, naphthalene and their aromatic homologs appear to be suitable for the above objective. These substances may control the width of the pore when they have access to the pore wall and can be selectively carbonized within the pore. Benzene with molecular thickness of 0.37 nm has been provided the necessary selectivity by preferential deposition and the most employed one (David

M.A. Ahmad (✉)
School of Chemical Engineering, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, Penang, Malaysia
e-mail: chazmier@eng.usm.my

et al. 2004). Hydrocarbons, such as methane, ethane, ethylene and acetylene form intermediate products during CVD step. Each of the intermediate products carbonized to produce heterogeneous deposition on the pore wall (Kawabuchi et al. 1996). As the result the entire pore wall was not as effectively coated.

The objective of this work was to produce CMSs from palm shell through three sequential stages; carbonization, activation and CVD technique. Palm shell is the by-product from oil palm industry in Malaysia. Currently, the palm shell has no specific technical uses and only a small portion is used as fuel to generate process steam in the palm-processing mill. Thus the palm shell based AC was prepared first by carbonization followed by steam activation. Then the AC pore mouth will be narrowed by using benzene vapour deposition technique. Benzene as carbon source for CVD is six-carbon organic with cyclic with highly chemical stability.

2 Experimental

2.1 Materials

The major material used in this study is palm shell of *tenera* type, which was obtained from a local oil palm mill. The methane, nitrogen, oxygen and carbon dioxide gases with high purity (>99.99%) were supplied by Malaysian Oxygen Ltd. Analytical grade of benzene was supplied by Merck Chemicals Ltd.

2.2 Preparation of CMS

The AC from palm shell was prepared by carbonization followed by steam activation. The apparatus and the preparation procedure are described elsewhere (Ahmad et al. 2007). The palm shell was ground and sieved to a particle size between 1.0 to 2.0 mm. Then, palm shell was carbonized at 830°C for 1 h under nitrogen flow before being activated with steam for 30–420 min. After the desired time elapsed, the reactor was cooled to room temperature under flowing nitrogen. The AC produced was discriminated by the degree of carbon burn-off, θ (wt%), which was calculated as follows:

$$\theta = \frac{W_i - W_t}{W_i} \times 100 \quad (1)$$

where W_i is the initial mass of the sample before activation and W_t is the mass of the sample at the end of activation. CVD was carried out by flowing nitrogen stream containing controlled amounts of benzene at 150 ml/min over the activated sample stored in a stainless steel reactor. The bed temperature was measured using a K-type thermocouple. The sample was first heated up in a stream of nitrogen until desired deposition temperature (600–800°C) was reached. A prescribed amount of benzene was supplied by a micro feeder into the nitrogen gas flow for a period of time. The weight gain of the sample was recorded as the difference between the sample weights after and before the treatment.

2.3 Characterization

All the samples were characterized by nitrogen adsorption at 77 K by using Micromeritics ASAP 2010 apparatus. The surface area was measured from the adsorption isotherms by using Brunauer-Emmett-Teller (BET) equation. The micropore volume was calculated using Dubinin-Radushkevich (DR) equation over a range of relative pressure of 1.1×10^{-5} to 0.02. Their molecular sieving properties were evaluated by measuring the adsorption of pure O_2, N_2, CO_2 and CH_4, volumetrically under ambient conditions. 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 at 1 s intervals thereafter. Kinetic data were obtained by using adsorption rate software in the same apparatus as in the characterization analysis.

3 Results and discussion

3.1 Activated carbons characterization

The AC burn-offs and surface areas were found to increase with activation temperature as shown in Table 1. This was due to the removal of the volatile matter and moisture from the palm shell structure. At high temperature and longer activation time, the diffusion of H_2O molecules into the interior became extensive, developing large amount of new pore, which contributed to high surface area (Kim et al. 2002). The deposit of tarry material was cleared and the carbon was exposed to the activation agent. The continuous development of microporosity takes place till the activation time of 250 min, beyond which the micropore volume starts to decrease indicating that the enlarging micropores into large

Table 1 Properties of activated carbons

Sample	Activation time (min)	Burn-off (%)	S_{BET} (m^2/g)	V_{mic} (ml/g)
AC30	30	16.1	575.9	0.2784
AC90	90	31.3	654.9	0.3767
AC160	160	45.1	980.2	0.3950
AC250	250	53.2	1104.0	0.4067
AC340	340	57.2	1302.3	0.3893
AC420	420	58.7	1318.7	0.3397

pores has begun as more carbon was removed (Gergova et al. 1994; Samaras et al. 1998).

This argument was supported by the analysis results of the adsorption isotherms as shown in Fig. 1. For ACs produced at activation time up to 250 min, the monolayer adsorption isotherm can be observed. These ACs can be classified as type I or microporous materials. Meanwhile the isotherms of the samples AC340 and AC420 indicated some undesirable mesoporosity development, which begins by the burn out of walls between adjacent micropores. These results suggest that the appropriate activated carbon for CMS production was sample AC250, which exhibits the largest microporous behaviour.

3.2 Benzene deposition

3.2.1 Effect of deposition temperature

In order to study the effect of deposition temperatures on CMSs properties, the deposition time and benzene concentration were fixed at 30 min and 30 vol.% benzene in nitrogen, respectively. As the deposition temperature increased, the weight gain increased whereas the surface area decreased as shown in Table 2. The micropore volume increased up to deposition temperature of 800°C beyond dropped at higher temperature. At low deposition temperature, the CVD seems to occur at pore wall, which resulted in low micropore volume.

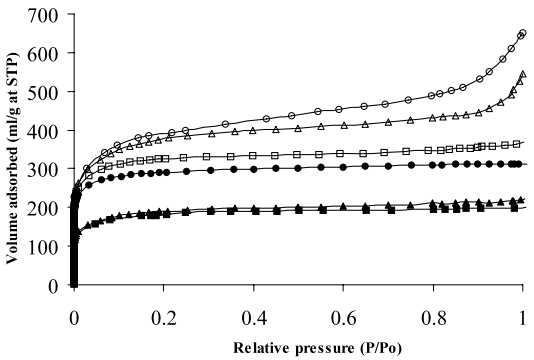

Fig. 1 Adsorption isotherm of activated carbon with different degree of burn-off; 16.1% (■), 31.3% (▲), 45.1% (●), 53.2% (□), 57.2% (△), 58.7% (○)

At 800°C, the micropore volume improved, which indicated that the CVD occur at the pore mouth without diffusion inside the pore wall (Freitas and Figueiredo 2001; De Salazar et al. 2005). In addition, some of the large pores narrow down to micropore regime. However at 900°C, the micropore volume dropped significantly due to the heterogeneous deposition, which blocked some of the pores (Kawabuchi et al. 1996).

Individual adsorption kinetics of O_2, N_2, CO_2 and CH_4 were carried out at 298 K. Figure 2 illustrates CMSs uptake curves of O_2 and N_2 whereas Fig. 3 shows the uptake curves of CO_2 and CH_4. All samples adsorbed all gases very rapidly within 10 secs. The sorption rates of all gases are found in the following order: $CO_2 > O_2 > N_2 > CH_4$. This order is in agreement with earlier studies by Vyas et al. (1994), Kim et al. (2002) and De Salazar et al. (2005). Sud-

Table 2 CMSs properties obtained at different deposition temperatures

Sample	Deposition temperature (°C)	Weight gain (mg/g)	S_{BET} (m^2/g)	V_{mic} (ml/g)
CMS600	600	38.4	932.3	0.381
CMS700	700	39.2	846.6	0.394
CMS800	800	41.3	704.1	0.412
CMS900	900	43.5	620.9	0.294

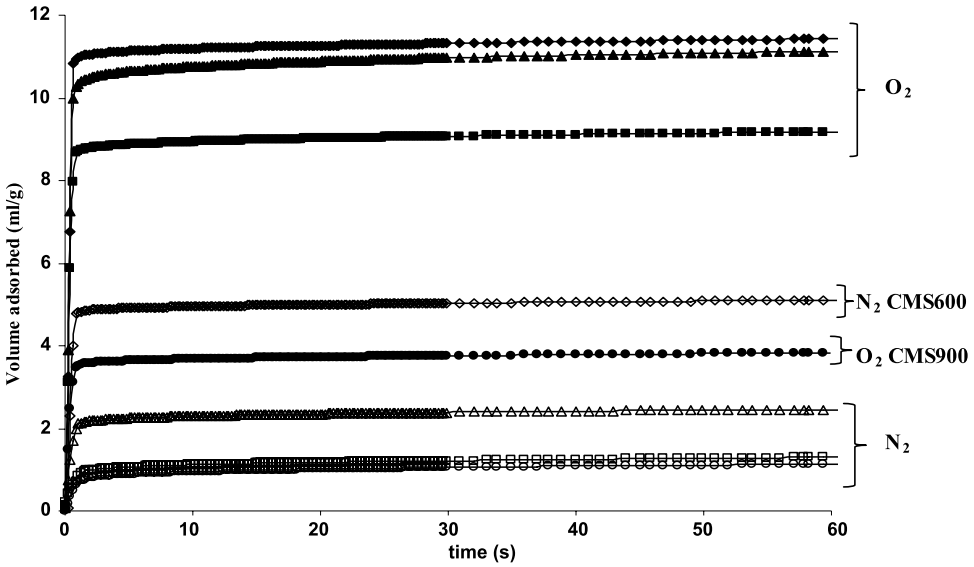

Fig. 2 Adsorption kinetics of O_2 and N_2 at 298 K; (*filled symbols*: O_2; *open symbols*: N_2); CMS600 (◆), CMS700 (▲), CMS800 (■) and CMS900 (●)

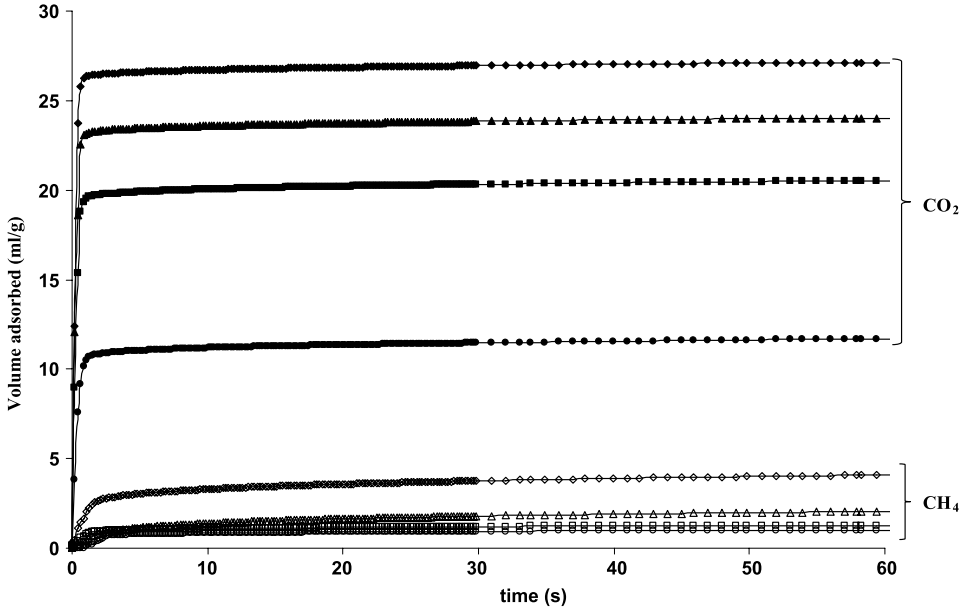

Fig. 3 Adsorption kinetics of CO_2 and CH_4 at 298 K; (*filled symbols*: CO_2; *open symbols*: CH_4); CMS600 (◆), CMS700 (▲), CMS800 (■) and CMS900 (●)

Table 3 Uptake values for gases and selectivities at 60 s

Sample	Uptake value (cm^3/g) at 60 s				S_{60}	
	O_2	N_2	CO_2	CH_4	O_2/N_2	CO_2/CH_4
AC250	12.43	11.74	29.8	9.11	1.06	3.27
CMS600	11.42	5.10	27.13	4.07	2.24	6.66
CMS700	11.12	2.46	24.03	2.04	4.52	11.80
CMS800	9.17	1.3	20.52	1.28	7.06	16.00
CMS900	3.82	1.13	11.69	1.01	3.39	11.55

Table 4 CMSs properties obtained at different deposition times

Sample	Deposition time (min)	Weight gain (mg/g)	S_{BET} (m^2/g)	V_{mic} (ml/g)
CMS800/15	15	28.4	892.4	0.3986
CMS800/30	30	41.3	704.1	0.4120
CMS800/45	45	42.2	555.0	0.4076
CMS800/60	60	42.6	410.8	0.3291

den decreased in O_2 and CO_2 uptakes have been observed for sample CMS900, which might reduce the O_2/N_2 and CO_2/CH_4 uptake ratios.

Table 3 is listed for better picture of the CMSs kinetic adsorption for various gas pairs. Sample AC250 was included for comparison. Almost five-fold increased in both O_2/N_2 and CO_2/CH_4 uptake ratios were observed for sample CMS800 compared to AC250. This indicated that porosity was being gradually narrowed. Benzene has smaller molecular thickness of 0.37 nm and lie down between the molecular sizes of CH_4 (0.38 nm) and CO_2 (0.33 nm) gases. The same phenomenon occurs for N_2 (0.36 nm) and O_2 (0.34 nm) gases. In addition, benzene molecules are planar in shape, contain aromatic structure and stable at high temperature (Kawabuchi et al. 1996; Javier and Mario 2004). However for sample CMS900, no improvement in the uptake ratios can be observed. This was due to the pore blockage by the pyrolytic benzene. At higher temperature, the deposition process being too fast and form uneven coating on the activated surface. Similar trend of uptake ratios have been reported for CMSs produced from coconut shell by Vyas et al. (1994) and Kim et al. (2002). Thus the most suitable deposition temperature for CVD is found to be at 800°C.

3.2.2 *Effect of deposition time*

The deposition temperature and benzene concentration were fixed at 800°C and 30 vol.% benzene in nitrogen, respectively in order to study the effect of deposition time. As the deposition time increased, the weight gain increased and surface area decreased as shown in Table 4. A slightly increased in micropore volume was observed up to 30 min of deposition time. Beyond that, the micropore volume dropped due to the excessive filling of the pores, which clogged some of the pores (David et al. 2004). The results obtained were in similar trend with previous work done by Nguyen and Do (1995) for CSM produced from macadamia nut shell.

Figure 4 illustrates uptake curves of O_2 and N_2 whereas Fig. 5 shows the uptake curves of CO_2 and CH_4 for CMSs produced at different deposition times. The adsorption kinetics for various gas pairs by the CMSs were summarized in Table 5. Up to 30 min of deposition time, the O_2 and CO_2 uptakes slightly decreased, but the uptake ratios was

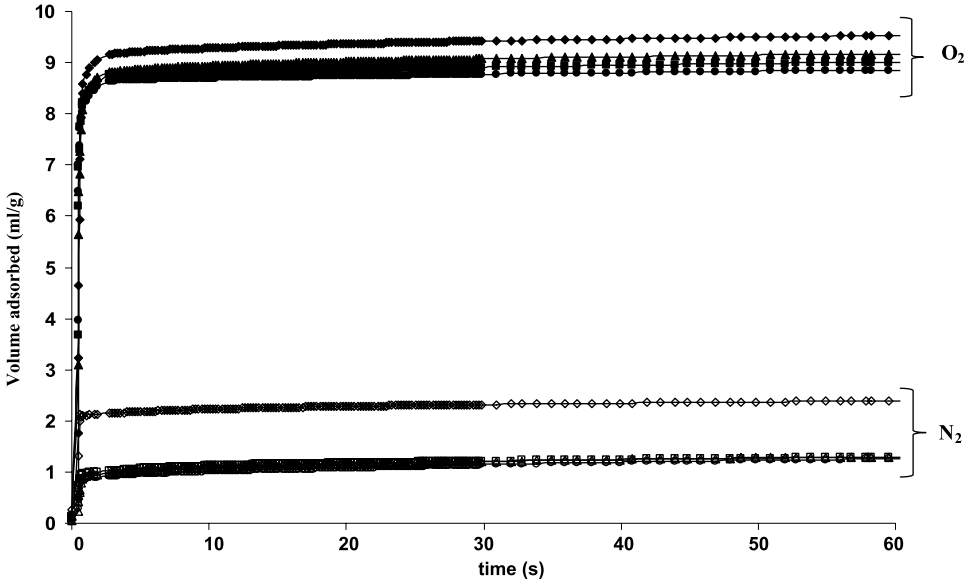

Fig. 4 Adsorption kinetics of O_2 and N_2 at 298 K; (*filled symbols*: O_2; *open symbols*: N_2); CMS800/15 (◆), CMS800/30 (▲), CMS800/45 (■) and CMS800/60 (●)

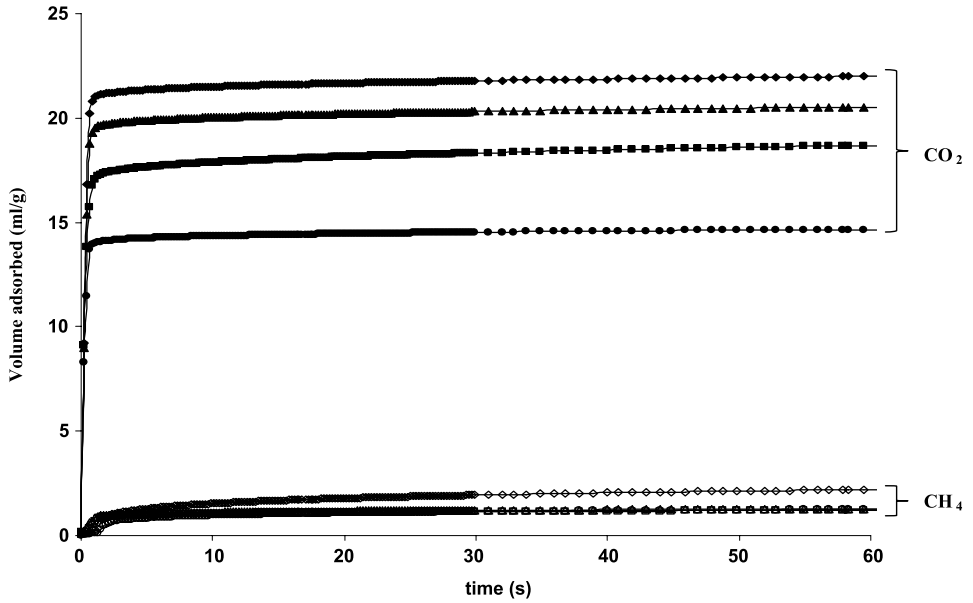

Fig. 5 Adsorption kinetics of CO_2 and CH_4 at 298 K; (*filled symbols*: CO_2; *open symbols*: CH_4); CMS800/15 (◆), CMS800/30 (▲), CMS800/45 (■) and CMS800/60 (●)

Table 5 Uptake values for gases and selectivities at 60 s

Sample	Uptake value (cm^3/g) at 60 s				S_{60}	
	O_2	N_2	CO_2	CH_4	O_2/N_2	CO_2/CH_4
AC250	12.43	11.74	29.8	9.11	1.06	3.27
CMS800/15	9.52	2.39	21.98	2.19	3.99	10.05
CMS800/30	9.17	1.30	20.52	1.28	7.06	16.00
CMS800/45	9.01	1.28	18.67	1.21	7.02	15.43
CMS800/60	8.75	1.25	14.66	1.25	7.00	11.72

improved. This improvement was due to the drastically decreased of N_2 and CH_4 adsorption rates. Beyond that, a rapid decreased in uptake for all gases takes place. Prolonged the deposition time possibly blockage the CMSs pores.

Table 6 CMSs properties obtained at various benzene concentrations

Sample	% vol. C_6H_6 in N_2	Weight gain (mg/g)	S_{BET} (m^2/g)	V_{mic} (ml/g)
CMS800/30/10	10	38.4	752.4	0.408
CMS800/30/20	20	40.8	733.9	0.410
CMS800/30/30	30	41.3	704.1	0.412
CMS800/30/40	40	41.5	681.3	0.412

3.2.3 The effect of benzene concentrations

The deposition temperature and time were fixed at 800°C and 30 min, respectively in order to study the effect of benzene concentrations on CMSs properties and gases uptake.

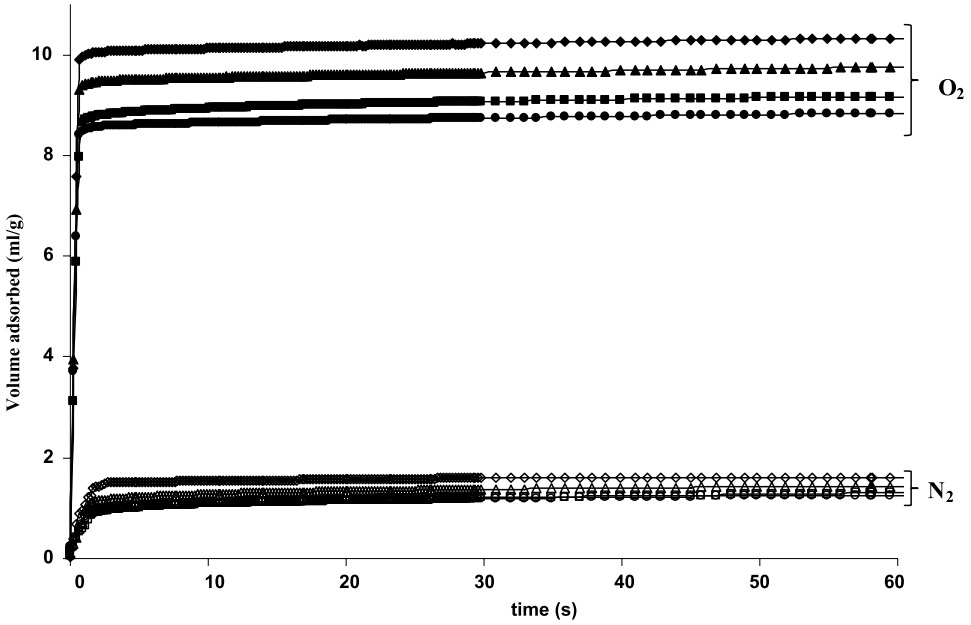

Fig. 6 Adsorption kinetics of O_2 and N_2 at 298 K; (*filled symbols*: O_2; *open symbols*: N_2); CMS800/30/10 (◆), CMS800/30/20 (▲), CMS800/30/30 (■) and CMS800/30/40 (●)

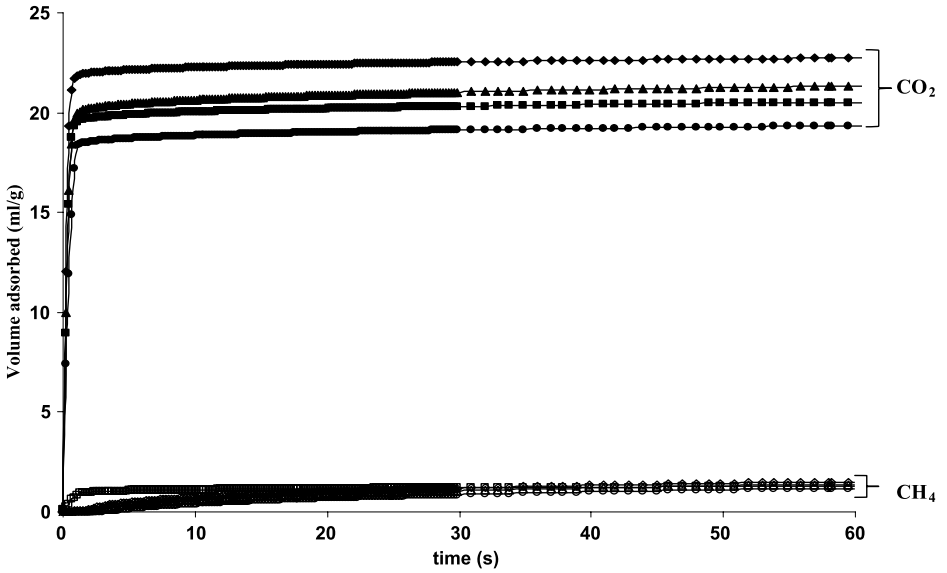

Fig. 7 Adsorption kinetics of CO_2 and CH_4 at 298 K; (*filled symbols*: CO_2; *open symbols*: CH_4); CMS800/30/10 (◆), CMS800/30/20 (▲), CMS800/30/30 (■) and CMS800/30/40 (●)

The weight gain and micropore volume were found almost constant and the surface area was slightly decreased with increased in benzene concentration as shown in Table 6. Figure 6 illustrates uptake curves of O_2 and N_2 whereas Fig. 7 shows the uptake curves of CO_2 and CH_4. The adsorption of all gases has almost attained equilibrium conditions at 60 s for all samples. In addition, the gases uptake for N_2 and CH_4 were small, indicating an excellent selectivity for separating O_2/N_2 and CO_2/CH_4. Table 7 is listed for kinetic adsorption for various gas pairs by the CMSs. Although the benzene concentration increased, the O_2/N_2 and CO_2/CH_4 uptake ratios were almost same. It seems that the effect of benzene concentration was not much significant towards the uptake ratios of O_2/N_2 and CO_2/CH_4 compared to the effect from deposition temperatures and times.

Table 7 Uptake values for gases and selectivities at 60 s

Sample	Uptake value (cm^3/g) at 60 s				S_{60}	
	O_2	N_2	CO_2	CH_4	O_2/N_2	CO_2/CH_4
AC250	12.43	11.74	29.8	9.11	1.06	3.27
CMS800/30/10	10.32	1.62	22.73	1.51	6.37	15.03
CMS800/30/20	9.75	1.44	21.32	1.38	6.77	15.42
CMS800/30/30	9.17	1.30	20.52	1.28	7.06	16.00
CMS800/30/40	8.84	1.26	19.36	1.21	7.02	16.00

4 Conclusions

Palm shell has been successfully used to prepare CMSs. The activated sample produced at burn-off 53.2% was found to

be suitable as precursor for CMSs production. The molecular sieving behaviour of CMSs was found to depend mostly on the deposition temperature and time. The most suitable deposition temperature, time and benzene concentration were 800°C, 30 min and 30 vol% benzene, respectively. At this point the uptake ratios for O_2/N_2 and CO_2/CH_4 were 7.06 and 16.0, respectively.

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References

Ahmad, M.A., Wan Daud, W.M.A., Aroua, M.K.: Synthesis of carbon molecular sieves from palm shell by carbon vapor deposition. J. Porous Mater. **14**(4), 393–399 (2007)

Braymer, T.A., Coe, C.G., Farris, T.S., Gaffney, T.R., Schork, J.M., Armor, J.N.: Granular carbon molecular sieves. Carbon **32**, 445–452 (1994)

David, E., Talaie, A., Stanciu, V., Nicolae, A.C.: Synthesis of CMS by benzene pyrolysis over microporous carbon materials. J. Mater. Process. Technol. **157**, 290–296 (2004)

De Salazar, C.G., Sepúlveda-Escribano, A., Rodríguez-Reinoso, F.: Preparation of CMS by pyrolytic carbon deposition. Adsorption **11**(1), 663–667 (2005)

Freitas, M.M.A., Figueiredo, J.L.: Preparation of CMS for gas separations by modification of the pore sizes of activated carbons. Fuel **80**(1), 1–6 (2001)

Gergova, K., Petrov, N., Eser, S.: Adsorption properties and microstructure of activated carbons produced from agricultural by-products by steam pyrolysis. Carbon **32**, 693–702 (1994)

Hu, Z., Vansant, E.F.: Synthesis and characterization of controlled micropore sized carbonaceous adsorbent produced from walnut shell. Microporous Mater. **3**, 603–612 (1995)

Javier, C.M., Mario, L.R.: Vapor-phase chemical equilibrium for the hydrogenation of benzene to cyclohexane from reaction-ensemble molecular simulation. Fluid Phase Equilib. **219**(2), 181–193 (2004)

Kawabuchi, Y., Kishino, M., Kawano, S., Whitehurst, D.D., Mochida, I.: Carbon deposition from benzene and cyclohexane onto active carbon fiber to control its pore size. Langmuir **12**(17), 4281–4285 (1996)

Kim, T.H., Vijayalakshmi, S., Son, S.J., Kim, J.D.: The pore mouth tailoring of coal and coconut char through acid treatment followed by coke deposition. J. Porous Mater. **9**, 279–286 (2002)

Nguyen, C., Do, D.D.: Preparation of CMS from macadamia nut shells. Carbon **33**(12), 1717–1725 (1995)

Reid, C.R., Thomas, K.M.: Adsorption kinetics and size exclusion properties of probe molecules for the selective porosity in a CMS used for air separation. J. Phys. Chem. **105**, 10619–10629 (2001)

Ruthven, D.M.: Principles of Adsorption and Adsorption Process. Wiley, New York (1984)

Samaras, P., Dabou, X., Sakellaropoulos, G.P.: Thermal treatment of lignite for carbon molecular sieve production. J. Therm. Anal. Calorim. **52**(3), 717–728 (1998)

Villar-Rodil, S., Navarrete, R., Denoyel, R., Albiniak, A., Parades, J.I., Martinez-Alonso, A., Tascon, J.M.D.: CMS cloths prepared by chemical vapor deposition of methane for separation of gas mixtures. Microporous Mesopores Mater. **77**(2), 109–118 (2005)

Vyas, S.N., Patwardhan, S.R., Vijayalakshmi, S., Ganesh, K.S.: Adsorption of Gases on carbon molecular sieves. J. Colloid Interface Sci. **168**, 275–280 (1994)