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Carbon dioxide and methane adsorption at high pressure on activated carbon materials

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Abstract Granular and monolith carbon materials were prepared from African palm shell by chemical activation with H_3PO_4, $ZnCl_2$ and $CaCl_2$ aqueous solutions of different concentrations. Adsorption capacity of carbon dioxide and methane were measured at 298 K and 4,500 kPa, and also of CO_2 at 273 K and 100 kPa, in a volumetric adsorption equipment. Correlations between the textural properties of the materials and the adsorption capacity for both gases were obtained from the experimental data. The results obtained show that the adsorption capacity of CO_2 and CH_4 increases with surface area, total pore volume and micropore volume of the activated carbons. Maximum adsorption values were: 5.77 mmol CO_2 g^{-1} at 273 K and 100 kPa, and 17.44 mmol CO_2 g^{-1} and 7.61 mmol CH_4 g^{-1} both at 298 K and 4,500 kPa.

Keywords Carbon dioxide · Methane · Adsorption · Activated carbon · High pressure

1 Introduction

The environmental problems caused by pollutant emissions from fossil fuel combustion have created an increasing interest for developing alternative solutions based on cleaner energies. From this perspective and a part from renewable energies, natural gas is considered as a cleaner fuel because of its lower emissions compared to oil and carbon. On the other hand, there is also an increasing interest in developing new selective materials for CO_2 capture and CH_4 adsorption, where porous carbon-based materials are good adsorbent candidates for this purpose (Carlson 2003; Giraldo and Moreno-Piraján 2009).

Adsorption processes are mature technologies being widely used based on the high performance of the adsorbent materials. The key for improving these processes relies on the development of new adsorbent solids with advanced properties, having high adsorption capacity and selectivity and low cost, tuned for specific applications (Drage et al. 2009). Activated carbon materials show a wide versatility and a low cost, being particularly attractive for CO_2 and CH_4 adsorption in capture/storage applications (Zhou et al. 2005).

Activated carbons in different forms (granular carbon particles, carbon cloths, carbon fibers and carbon monoliths) can be used as adsorbents for gases, metals, organic vapours, etc. (Ahmad et al. 2010; Dominique et al. 2009; Mohan et al. 2008). Many studies were made about the preparation of activated carbon and further characterization. A large number of precursors of lignocellulosic origin, mineral, artificial, which have been subjected to chemical activation processes with substances as: H_3PO_4, $ZnCl_2$, $CaCl_2$, $AlCl_3$, KOH or physical processes with CO_2 or water vapor. Each activating agent leads to the production of carbonaceous materials with different textural characteristics. In several studies, palm shell has been used as precursor for obtaining carbon materials, which have been used for adsorption of methane, 2,4,6-trichlorophenol, lead. Dyes, SO_2 and NO_x, CO_2, phenol and others (Arami-Niya et al. 2012; Arami-Niya et al. 2011; Tan et al. 2008, 2009; Sumathi et al. 2010; Issabayeva et al. 2008; Jia and Lua 2008).

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When activated carbons are used for gas phase adsorption, one of the main targets is to get the highest apparent density of the adsorbent material to obtain the largest volumetric adsorption capacity, which would mean in the case of methane adsorption the highest energy density. This can be accomplished by reducing the volume space not efficient for gas storage (macro- and mesopores) and keeping a high micropore volume. This volume space reduction requires an appropriate compactation, which can be based on the use of powder mixtures of different grain size, uni-axial compression of powder with or without additives, or by preparing compact monoliths. The preparation of activated carbon monoliths (ACMs) is an interest option to reduce the interparticle volume space and increase the apparent density of the material (Rodríguez-Reinoso et al. 2004; Jordá-Beneyto et al. 2008). Besides, monolith cylindrical structures can be arranged in a uniform pack that allows an optimal use of the tank volume, and have very good mechanical properties, being hard, friction resistant and easy to handle.

Also, the preparation of ACMs has resulted in numerous studies on methodologies for compacting of precursors or carbon, and binder substances which permit binding of the particles during pressing. However, these compounds produce a partial blockage of the porosity of the material. For this reason, in recent years various studies have been performed to allow the synthesis of these structures without the use of binders (Jordá-Beneyto et al. 2008; Rodriguez-Reinoso et al. 2004; Giraldo and Moreno-Piraján 2009). One of the methods disclosed for the synthesis of monoliths without binders is the use of an activating agent that can interact with the lignocellulosic precursor to produce dehydration, condensation and degradation reactions of biopolymers, and the substances produced in this process remain in solution to act as binders during the pressing.

In accordance with the above, the aims of this work is to make a study of carbon dioxide and methane adsorption at high pressure on granular and monolith carbon materials, that were prepared by chemical activation of African palm shell, using three different chemical products in aqueous solution: H_3PO_4, $ZnCl_2$ and $CaCl_2$. Samples were characterized by N_2 adsorption at 77 K and by CO_2 adsorption at 273 K. The adsorption capacity of CO_2 and CH_4 at 298 K and 4,500 kPa was measured for selected materials which showed the best textural properties.

2 Experimental

Carbon materials were prepared from African palm shell as a lignocellulosic precursor, which was treated by impregnation with aqueous solutions of phosphoric acid, zinc chloride or calcium chloride. The impregnation was carried out by using 2 mL of solution per gram of material precursor, with solutions of different concentrations, as shown in Table 1. The samples were named according to the activating species used: H_3PO_4 (sample series GP and MP), $ZnCl_2$ (sample series GZn y MZn) y $CaCl_2$ (sample series GCa y MCa), G and M referring to Granulate and Monolith, respectively. The following number in each sample name represents the concentration of the activating species, according to values shown in Table 1. The synthesis of honeycomb monoliths required an additional compactation step, using a home-made uniaxial press that is shown in the Fig. 1. The methodology employed consists in loading the impregnated precursor in the mold, then heated until a temperature of 423 K and then applying a high pressure of 44,826 kPa during 0.5 min.

The resulting monoliths were cylindrical with about 1.5 cm diameter and 8 cm height, each with seven parallel channels of $\sim$3 mm diameter along the cylindrical axis. Table 1 shows the synthesis conditions for all series of materials.

The textural properties of the synthesized monoliths were analyzed by using N_2 adsorption at 77 K in a volumetric system (Quantachrome, Autosorb 3-B). Previous degasification of the samples was carried out at 523 K for 24 h reaching a pressure of 1×10^{-4} kPa. Micropore volume, V_0 (N_2), was obtained by applying Dubinin–Radushkevich model to the nitrogen adsorption data. Total pore volume, V_t, was obtained from the amount adsorbed at a relative pressure P/P^0 of 0.99, while the mesopore volume, V_{meso}, was obtained from the difference between the total pore volume and the micropore volume (Martín 1988). The external surface area was evaluated from scanning electron microscopy measurements for each carbon sample at different magnifications. Initially the carbon monolith was placed in a holder and a thin layer of gold was deposited on the surface under low pressure (10^{-4} Torr). The morphology was studied using a scanning electron microscope SEM JEOL JSM 6510 equipment at an accelerating voltage of up 30 kV.

Carbon dioxide and methane adsorption measurements were carried out in a volumetric adsorption equipment at 298 K, until a pressure of 4,500 kPa. Previous degasification of the samples was done, maintaining the samples for 3 h at a pressure of 1.145×10^{-7} kPa. After degasification, small amounts of each gas (CO_2 and CH_4) were introduced and the equilibrium pressure was then measured, with equilibrium times of about 3 min. This time was checked to be sufficient to reach equilibrium conditions. Pressure sensors used were measuring pressures in the range 0–6,000 kPa.

The equation of state was used to evaluate the fluid phase density and thus calculation of the number of moles of each gas.

Table 1 Synthesis conditions of carbon samples

Parameter	GP and MP Series	GZn and MZn Series	GCa and MCa Series
Activating agent	H_3PO_4	$ZnCl_2$	$CaCl_2$
Concentrations (wt%)	32, 36, 40, 48	32, 36, 40, 48	2, 3, 5, 7
Impregnation	358 K, 2 h	358 K, 7 h	358 K, 7 h
Drying	393 K, 6 h	393 K, 6 h	393 K, 6 h
Carbonization	723 K, 2 h	773 K, 2 h	1,073 K 6 h
	N_2 (80 mL min^{-1})	N_2 (80 mL min^{-1})	CO_2 (100 mL min^{-1})
	1 K min^{-1}	1 K min^{-1}	3 K min^{-1}
			Followed by 873 K, 2 h, N_2[a]
Washing	Hot distilled water until neutral pH	Hot HCl 0.01 M followed by hot distilled water until neutral pH	Hot HCl 0.01 M followed by hot distilled water until neutral pH
Storage	Plastic containers	Plastic containers	Plastic containers
	N_2 atmosphere	N_2 atmosphere	N_2 atmosphere

[a] Purge flow to eliminate excess of CO_2

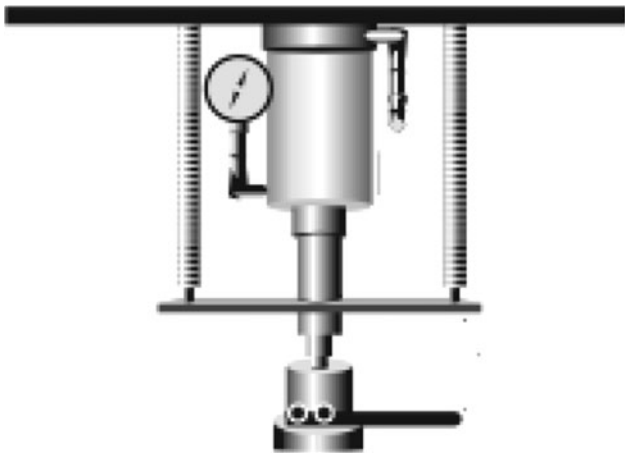

Fig. 1 Uniaxial press employed in this work

3 Results and discussion

3.1 Characterization of materials

Figure 2 shows SEM images of the MCa2 sample (monolith carbon activated with 2 % $CaCl_2$ solution) where the hexagonal channels of about 3 mm can be observed (Fig. 2a). The considerable degradation of the external surface produced during activation and thermal treatment of the material can be appreciated in Fig. 2b. Moreover in this figure it is possible to observe the irregular porous framework of an activated carbon.

A total number of 24 samples were prepared and characterized by N_2 adsorption at 77 K and CO_2 adsorption at 273 K, as mentioned, obtaining surface areas and pore volumes in the range 161–1,700 m^2 g^{-1} and 0.09–0.64 cm^3 g^{-1}, respectively. These values can be compared with those reported in work previously published (Ioannidou and Zabaniotou 2007). Samples with the best textural properties: surface area and pore volume were selected to study their adsorption properties for CO_2 and CH_4 capture. Figure 3 shows the N_2 adsorption isotherms of the selected materials. Adsorption isotherms of samples activated with phosphoric acid are type I, according to IUPAC classification (Sing et al. 1985), having a considerable microporosity. The adsorption isotherm of sample named GP48 (granular particles activated with 48 % H_3PO_4 solution) shows a more open curvature at low relative pressures ($P/P^0 < 0.1$), which indicates a wider pore size distribution in the small pore size region, while isotherm of sample MP48 (equivalent sample with monolith structure) shows a curvature closer to a step pattern in the same region, characteristic of a narrower pore size distribution. Similarly, carbon materials activated with $ZnCl_2$ are clearly microporous with isotherms corresponding to type Ib, showing a narrow pore size distribution. Besides, the isotherms of these materials seem to reach a horizontal plateau above $P/P^0 \sim 0.2$, which indicates that mesoporosity is practically non-existing. On the other hand, adsorption isotherms of GCa3 sample are type IV, showing a H4 hysteresis cycle according to IUPAC, which is characteristic of microporous solids with a slit-type of pore. Finally, MCa2 monolith sample shows an isotherm of type I with a closed curvature, corresponding to a narrow pore structure.

Table 2 summarizes the textural properties of the selected carbon samples. It can be observed that the volume of narrow micropores (V_n) obtained from CO_2 adsorption isotherms at 273 K is smaller than the total micropore volume determined by N_2 adsorption (V_0), which corresponds to pores smaller than 2 nm. This result shows the absence of kinetic restrictions for N_2 accessibility to narrow micropores. Some carbon samples show very close values of these two parameters (V_n and V_0), which reflects a narrow pore size distribution.

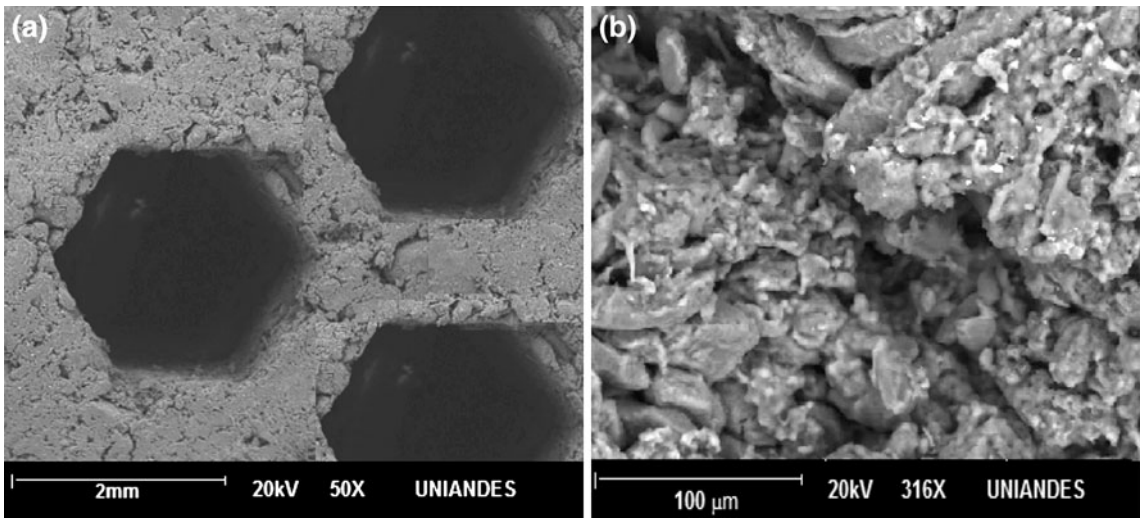

Fig. 2 SEM images of MCa2 sample: **a** Parallel channels of the monolith; **b** External surface

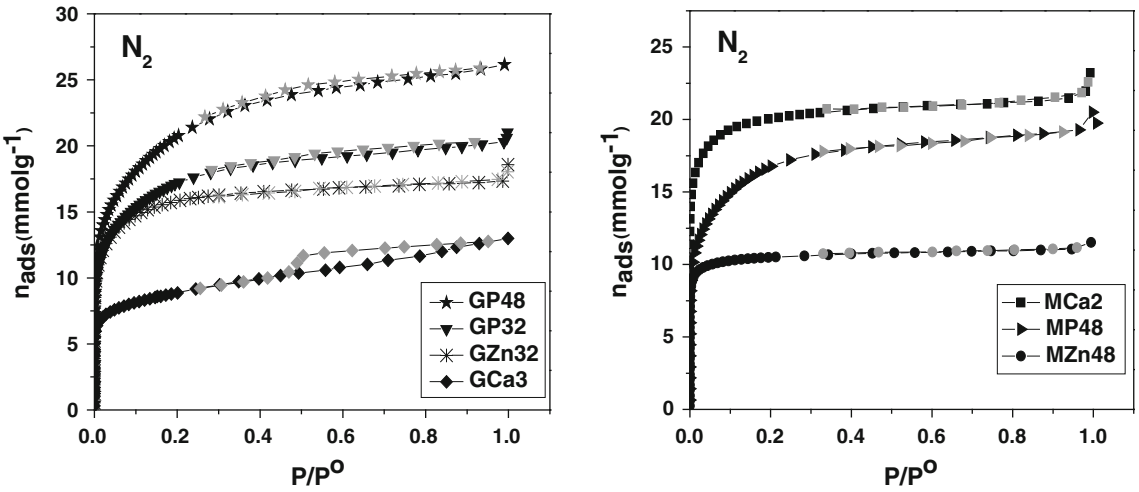

Fig. 3 N_2 adsorption isotherms of carbon samples a 77 K

Additionally, carbon samples activated with H_3PO_4 have the largest mesopore volume (V_{meso}), as a result of the formation of metaphosphate species during activation, that later on, when eliminated from the carbon structure in the calcination step, produce larger volume pores and heterogeneity (Suarez-García et al. 2002).

CO_2 isotherms at low pressures up to $P/P^0 = 0.03$ are shown in Fig. 4, a pressure range where information about the ultramicroporosity (pores smaller than 0.7 nm) can be obtained. Samples corresponding to MCa2 y GP48 present the largest narrow micropore volume (V_0, V_n) and therefore show the highest CO_2 adsorption. Other adsorbents with a higher ultramicroporosity, like MZn48 sample ($V_0/V_t = 0.97$), do not adsorb the same amount of CO_2 due to its low surface area value. So, it can be said that for CO_2 adsorption it is necessary not only a high narrow micropore volume but also a high surface area.

3.2 Storage capacity for methane and carbon dioxide

Adsorption capacity data of CO_2 and CH_4 for the selected activated carbon materials are presented in Table 3. As observed, adsorption values for CO_2 at 273 K and 100 kPa are in the range 3.00–5.77 mmol CO_2 g^{-1}, and for CO_2 and CH_4 at 298 K and 4,500 kPa are 8.62–17.44 mmol CO_2 g^{-1} and 4.16–7.61 mmol CH_4 g^{-1}, respectively.

Figure 5 shows the adsorption isotherms of CO_2 and CH_4 at high pressure. It appears that the activated carbon samples have better adsorption capacity for CO_2, since the materials adsorb up to 2.7 times more CO_2 than CH_4 in the same P, T conditions. This behavior can be due to the molecule size of the two adsorbates while the CO_2 has a kinetic diameter of 0.33 nm which allows easy access to a large proportion of the porosity of the samples, CH_4 presented kinetic constraints by size of 0.38 nm which is evidenced in a decrease of the gas

Table 2 Surface area and pore volume of activated carbon materials obtained from N_2 adsorption isotherms at 77 K and CO_2 adsorption isotherms at 273 K

N_2 adsorption data at 77 K						CO_2 adsorption data at 273 K
Sample	S_{BET} (m^2 g^{-1})	V_o (cm^3 g^{-1})	V_{meso} (cm^3 g^{-1})	V_t (cm^3 g^{-1})	V_o/V_t	V_n (cm^3 g^{-1})
GP32	1,407	0.50	0.23	0.73	0,68	0.34
GP48	1,685	0.58	0.33	0.91	0,64	0.42
MP48	1,368	0.48	0.18	0.66	0,73	0.32
GZn32	1,314	0.50	0.10	0.60	0,83	0.30
MZn48	924	0.37	0.01	0.38	0,97	0.36
GCa3	714	0.29	0.15	0.44	0,65	0.28
MCa2	1,700	0.64	0.10	0.74	0,85	0.43

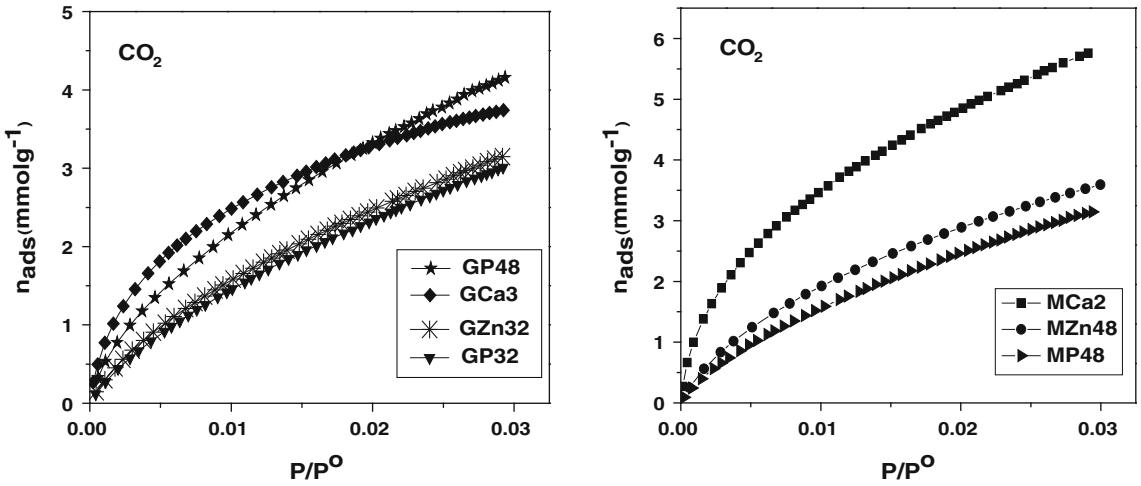

Fig. 4 CO_2 adsorption isotherms of carbon samples at 273 K

Table 3 Adsorption capacity of CO_2 (mmol g^{-1}) at 273 K and 100 kPa and also of CH_4 and CO_2 (mmol g^{-1}) at 298 K and 4,500 kPa on the carbon samples selected

Sample	Storage capacity (mmol CO_2 g^{-1}) 100 kPa and 273 K	Storage capacity (mmol CO_2 g^{-1}) 4,500 kPa and 298 K	Storage capacity (mmol CH_4 g^{-1}) 4,500 kPa and 298 K
GP32	3.00	13.18	5.67
GP48	4.16	16.41	6.02
MP48	3.15	12.44	5.43
GZn32	3.14	11.31	5.26
MZn48	3.59	11.01	4.98
GCa3	3.74	8.62	4.16
MCa2	5.77	17.44	7.61

adsorption. Clearly, the adsorption process does not only depend on equilibrium, but also on accessibility of the adsorbate to the porous network of the material. Several theoretical studies have shown that the optimum pore size for methane storage is ~0.8 nm, which corresponds to a distance between pore walls of about twice the molecule diameter (Alcañiz-Monge et al. 1997). Thus, with a predominant pore size of the carbon samples in the ultramicroporosity range (0.7 nm), CH_4 adsorption would be hindered. These results lead to the conclusion that these activated carbon materials could be useful for gas separation of carbon dioxide and methane in adsorption separation processes.

Other studies on CO_2 adsorption using different carbon materials, zeolites, and metal–organic frameworks (MOF) have reported adsorption capacities as for example 8.63 mmol CO_2 g^{-1} at 273 K and 100 kPa on carbon molecular sieves of surface area S_{BET} = 3,100 m^2 g^{-1} and pore volume V_n higher than 1.40 cm^3 g^{-1} (Wahby et al. 2010). Compared to these data, the adsorption capacity values of 5.77 mmol CO_2 g^{-1} at 273 K and 100 kPa obtained in this study for carbon materials with moderate surface areas and pore volumes can be considered as satisfactory.

Similarly, the maximum adsorption capacity of CO_2 at 298 K and 4,500 kPa obtained in this study (MCa2 material)

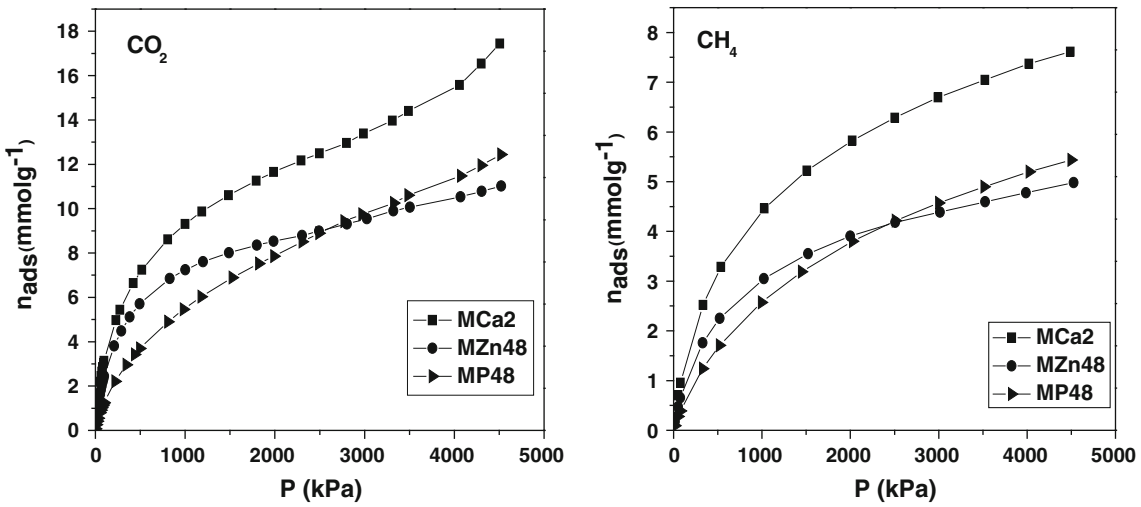

Fig. 5 Adsorption isotherms of CO_2 and CH_4 at 298 K and 4,500 kPa on the carbon samples

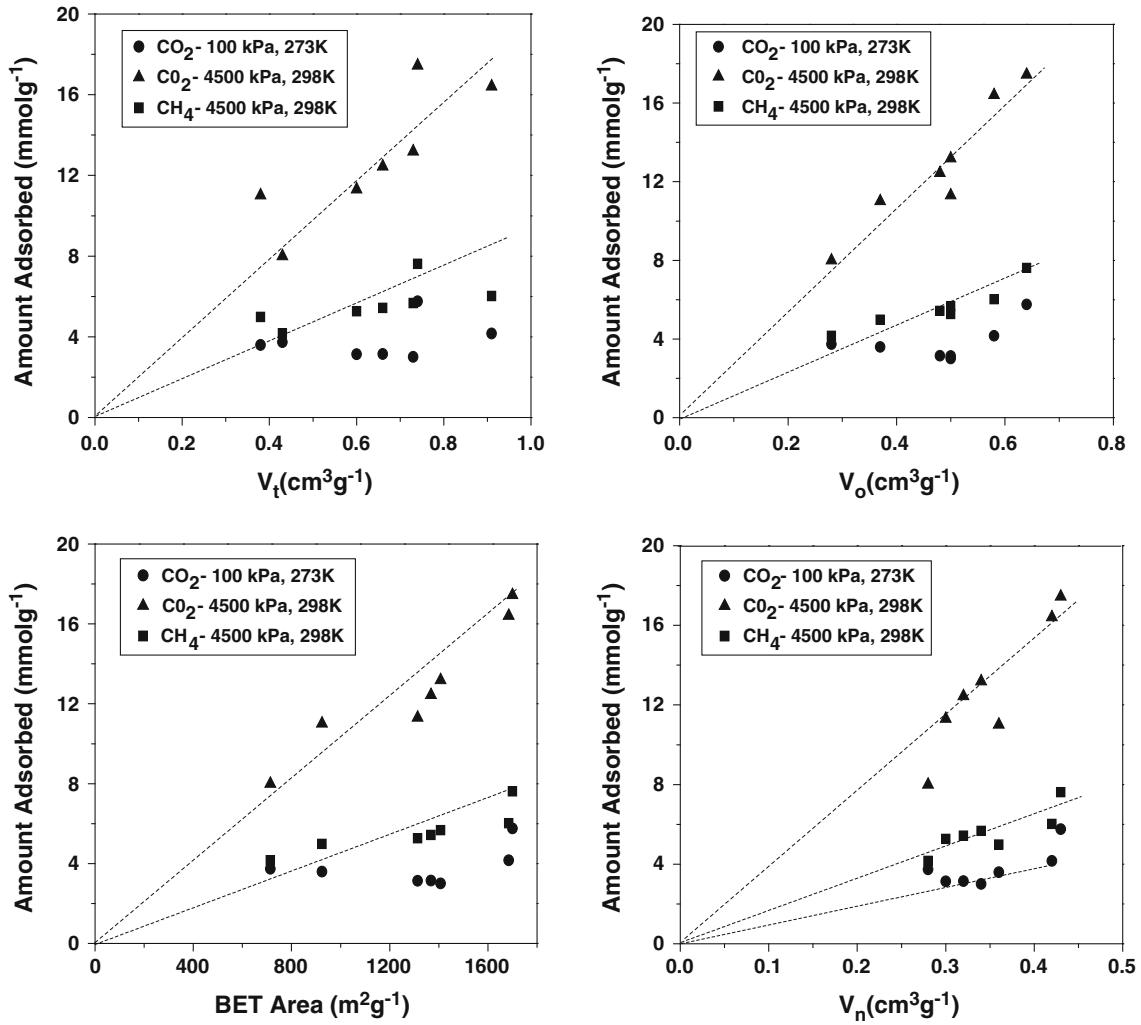

Fig. 6 Correlation between the storage capacity of CO_2 and CH_4 and the textural properties of the carbon materials: **a** Total pore volume (V_t); **b** micropore volume (V_o); **c** BET surface area, and **d** the narrow micropore volume (V_n)

was 17.44 mmol CO_2 g^{-1}. This value is low compared to that for materials as: metal–organic frameworks (MOF-107), IRMOF-1, Silica (MCM-41-100), activated carbons (MaxsorbAC, NoritAC) and Zeolite (13X) (Wahby et al. 2010; Millward and Yaghi 2005; Belmabkhout et al. 2009; Himeno et al. 2005; Cavenati et al. 2004). Under these experimental conditions, a storage capacity was reported of 40 mmol CO_2 g^{-1} in MOF-107 with BET area of 4,508 m^2 g^{-1}. However, our MCa2 monolith surpasses others materials as MCM-41-100 that stores 14.70 mmol CO_2 g^{-1}, Zeolite 13X with 7.37 mmol CO_2 g^{-1} and carbonaceous material NoritAC with 11.28 mmol CO_2 g^{-1} (Wahby et al. 2010; Millward and Yaghi 2005; Belmabkhout et al. 2009; Himeno et al. 2005; Cavenati et al. 2004).

A relationship was established between adsorption capacity and the textural properties (V_t, V_o, V_n, S_{BET}) for each carbon material, as shown in Fig. 6. As observed, storage capacity of CO_2 at 298 K and 4,500 kPa is determined by the pore volumes V_t, V_o, V_n and the BET surface area, due to that is evident the increase of CO_2 adsorption capacity with the increment in these parameters. Similarly, storage capacity of CH_4 at 298 K and 4,500 kPa shows an analogous trend. However, the adsorption capacity of CO_2 at 273 K and 100 kPa in the carbon adsorbents does not show any clear relationship with V_t, V_o, and S_{BET}, although a dependence with V_n is observed, the narrow micropore volume. It should be noted that the dotted lines in the Figures, show only a tendency of data.

4 Conclusions

Several activated carbons were prepared by impregnation of African palm shell with H_3PO_4, $ZnCl_2$ and $CaCl_2$ aqueous solutions. The seven selected materials with the best textural properties were tested for CO_2 and CH_4 adsorption. Surface area and pore volume of these materials were as high as 1,700 m^2 g^{-1} and 0.64 cm^3 g^{-1}, respectively, being the carbon sample activated with calcium chloride and with a monolith structure, MCa2, the best material for gas adsorption. Under the experimental conditions studied, adsorption capacity of CO_2 and CH_4 is related to the surface area and pore volume of the materials. The activated carbon materials obtained, in spite of their moderate values of surface area and pore volume, showed gas adsorption capacities at low pressure up to 5.77 mmol CO_2 g^{-1} (273 K, 100 kPa) and at high pressure up to 17.44 mmol CO_2 g^{-1} and 7.61 mmol CH_4 g^{-1} (298 K, 4,500 kPa).

Finally, the results obtained show that for activated carbons with a high microporosity and relatively low mesoporosity (GZn32, MZn48, GCa3, MCa2), monolithic structures seem to favor CO_2 and CH_4 adsorption, whereas for those carbons with a larger proportion of mesopores (GP32, GP48, MP48) the major contribution to adsorption comes from the pore size distribution regardless of the granular or monolith structure of the material.

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