

# Modification of activated carbon porosity by pyrolysis under pressure of organic compounds

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**Abstract** Co-pyrolysis at relatively low temperature (673 K) and high pressure (10 MPa), using three organic compounds, was used to modify the porosity of the two ACs. The co-pyrolysis is effective for the modification of the porosity of an AC, and the efficiency depends on the organic compound used. The differences found are consequence of the chemical composition of the organic precursor. High pressure pyrolysis produces beneficial results when an organic compound that volatilizes during the preparation is used. Conducting pyrolysis at low temperature permits improved control of the porosity because the rate of gasification can be more tightly controlled.

**Keywords** Activated carbon · Microporosity

## 1 Introduction

Activated carbons (ACs) are porous solids with interesting properties such as high thermal stability, high hydrophobic character and high chemical resistance. One of the most relevant characteristics of these materials is its versatile pore size distribution (Bansal et al. 1988). The pore size distribution is a function of several parameters, of which the most relevant are: the carbon precursor (Foley 1995), the pretreatment and carbonization process (Mackay and Roberts 1982; Vyas et al. 1993), and the activation process (Lozano-Castelló et al. 2002; Patrick and Arnold 1995). In general, all materials that after pyrolysis yielding a high carbon

content carbonized could be used as ACs precursor. Thus, coals, pitches, agricultural by-products, polymeric materials (phenol-formaldehyde resins, PAN, PVC), tires, sucrose, etc. have been used as ACs precursor, being coals and agricultural by-products the most widely used by industry. Usually, the ACs obtained from these precursors show a high pore volume but, also, a wide pore size distribution (containing micropores, meso and macropores).

In order to obtain ACs with a narrow pore size distribution, different post-treatments have been developed (Armor 1991; Cabrera et al. 1993; Chihara and Suzuki 1979; David et al. 2004; Freitas and Figueiredo 2001; Hu and Vansant 1995; Jüntgen et al. 1981; Kawabuchi et al. 1998; Miura et al. 1991; Mochida et al. 1995; Moreira et al. 2001; Orfanoudaki et al. 2003; Prasetyo and Do 1999; Toda et al. 1972; Verma and Walker 1990, 1992; Verma 1991; Walker et al. 1966): heat treatment, carbon deposition—from gas or from pyrolysis of impregnated organic substances—, controlled gasification and plasma. However, most of these methods need microporous materials with low meso and macroporosity (Armor 1991; Verma 1991) as precursors. In the industry, the most used method is the carbon deposition during carbonization at 673–1273 K on an organic compounds impregnated AC at atmospheric pressure (Miura et al. 1991; Walker et al. 1966). Bitumen, coal tar pitch, phenol-formaldehyde resins, cresol oil or benzene are the most widely used organic compounds.

On the other hand, for carbon-carbon composites preparation a similar carbonization process is used, but, usually, high pressure is utilized to obtain higher carbon yield (Hüttinger 1988; Nakao et al. 1995) than at atmospheric pressure (Ayache et al. 1990; Washiyama et al. 1988).

Taking into account the above comments, the use of pressure to modify the AC porosity by the carbon deposition from organic compounds method would be interesting. So,

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the main objective of this work is to study the porosity modification of ACs by organic compounds (added before pyrolysis) during pyrolysis at high pressure (10 MPa) and low temperature (673 K).

## 2 Experimental

### 2.1 Preparation of samples

#### 2.1.1 Activated carbon precursors

In order to analyse the influence of the ACs porosity, two ACs were used: a granular char prepared from a phenol-formaldehyde resin (denoted A) (Román-Martínez et al. 1996) and a commercial AC obtained from a coal (Coal Corporation of Victoria-CCV, denoted C). Table 1 summarizes the porous texture of these materials.

#### 2.1.2 Impregnation and pyrolysis treatments

Three organic compounds were used (n-nonane, ethylene glycol and sucrose) and, in sample the nomenclature, a symbol indicating the organic precursor (N for nonane, E for ethylene glycol and S for sucrose) was added. For impregnation

step, a 1 g AC/100 cc organic ratio compounds was used, but, for sucrose water saturated solution was employed. After impregnation, samples were thermally treated ( $N_2$  atmosphere at 10 MPa) in an autoclave at 673 K for 15 minutes (sucrose impregnated samples were previously dried). In this paper, these samples are denoted as “pyrolysed samples”. Finally, for comparative purpose, the thermal treatment was also carried out in a horizontal furnace using  $N_2$  at atmospheric pressure.

#### 2.1.3 Heat treatments of pyrolysed samples

In order to analyse the thermal stability of the carbon deposit on pyrolysed samples, a heat treatment in  $N_2$  (heating rate 10 K/min) until 1273 K was performed. These sample are denoted in the text as “carbonized samples” and “T” was added to the nomenclature. Additionally, sample CS was heat treated in  $N_2$  at two intermediate temperatures, 723 K (sample CS7T) and 773 K (sample CS8T). Finally, sample CS was heat treated in air at 673 K for 5 minutes (sample CS5A) or 15 minutes (sample CS15A).

As a summary, Table 2 shows the nomenclature of all samples and the corresponding heat treatment conditions used.

**Table 1** Porous texture of the two selected activated carbons

Pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	Total micropores/ $V_{N_2}$	Narrow micropores/ $V_{CO_2}$	Mesopores
A	0.25	0.27	0.39
C	0.64	0.44	0.20

**Table 2** Nomenclature of samples

Nomenclature	AC	Organic compound	Heat treatment conditions
AS	A	Sucrose	Pyrolysis under pressure & Heat Treatment (at 1273 K in $N_2$ atmosphere)
AN		n-nonane	
AE		Ethylenglycol	
AST		Sucrose	
ANT	C	n-nonane	Pyrolysis under pressure & Heat Treatment (at 1273 K in $N_2$ atmosphere)
AET		Ethylenglycol	
CS		Sucrose	
CN		n-nonane	
CE		Ethylenglycol	Pyrolysis under pressure & Heat Treatment (at 1273 K in $N_2$ atmosphere)
CST		Sucrose	
CNT		n-nonane	
CET		Ethylenglycol	
CS7T		Sucrose	Pyrolysis under pressure & Heat Treatment (at 723 K in $N_2$ atmosphere)
CS8T			Pyrolysis under pressure & Heat Treatment (at 773 K in $N_2$ atmosphere)
CS5A			Pyrolysis under pressure & Heat Treatment (at 673 K in $O_2$ atmosphere for 5 minutes)
CS15A			Pyrolysis under pressure & Heat Treatment (at 673 K in $O_2$ atmosphere for 5 minutes)

## 2.2 Characterisation

### 2.2.1 Porous texture characterization

Porous texture analysis was carried out by N<sub>2</sub> adsorption at 77 K and CO<sub>2</sub> adsorption at 273 K using an automatic system (Autosorb 6, Quantacrome). The samples were degassed at 600 K under 1 Pa vacuum during 6 hours. The narrow micropores, the total micropores and the mesopore volumes were calculated as follows (Rodríguez-Reinoso and Linares-Solano 1988): (i) the narrow micropores volume (pore size <0.7 nm) was calculated by applying the DR equation to the CO<sub>2</sub> adsorption data at relative pressures lower than <0.015; (ii) the total micropore volume, i.e., including both narrow micropores (CO<sub>2</sub> DRs) and the supermicropores (pore size <2 nm), by applying the Dubinin-Radushkevich equation (Dubinin 1989) the N<sub>2</sub> adsorption data at relative pressures lower than <0.14 and (iii) the volume of mesopores, by applying the t-methods to the N<sub>2</sub> adsorption data (Gregg and Sing 1967).

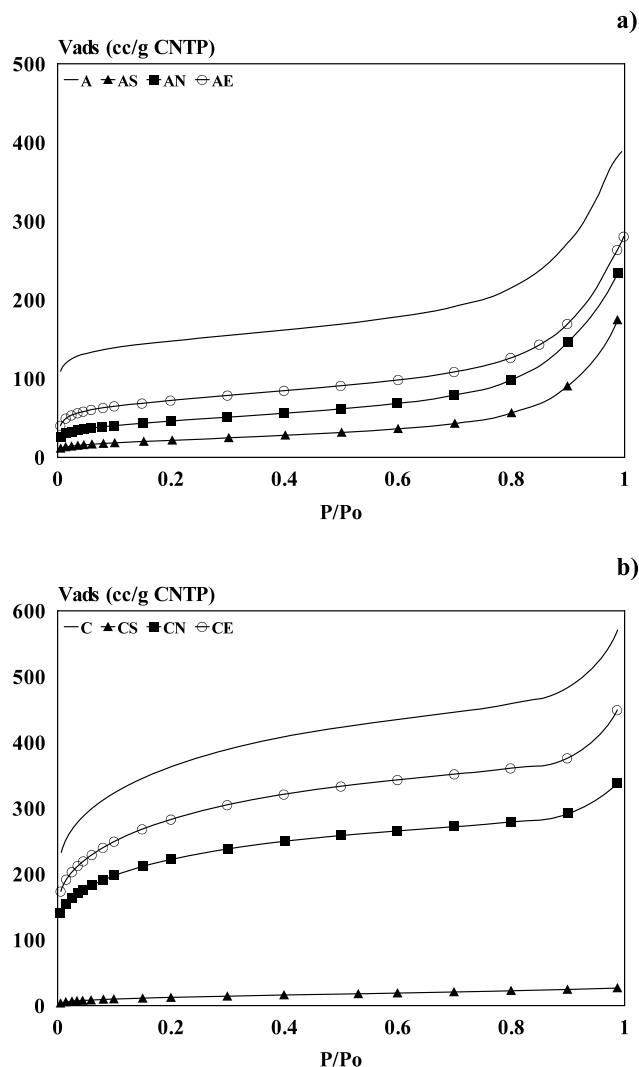
### 2.2.2 Adsorption kinetics studies

Adsorption kinetic studies using CH<sub>4</sub> and CO<sub>2</sub> were carried out to determine the ACs molecular sieve properties. For comparative purpose, a commercially molecular sieve (Takeda 3A) was also studied. Adsorption kinetics of CH<sub>4</sub> and CO<sub>2</sub> were carried out in a constant volume DMT high-pressure microbalance (Sartorius 4406) at 298 K and 0.1 MPa. The samples (0.1 g) were previously degassed overnight at 523 K under vacuum (10<sup>−5</sup> bar). The experimental results were corrected considering the buoyancy effects related to the displacement of gas by sample, the sample holder, the adsorbed phase and pan (Agarwal and Schwarz 1988).

## 3 Results

### 3.1 Characterization of the porous texture of pyrolysed samples

Figures 1 and 2 show the N<sub>2</sub> and CO<sub>2</sub> adsorption isotherms for raw (A, C) and pyrolysed ACs (AS, AN, AE, CS, CN, CE). The N<sub>2</sub> isotherms slope for raw AC reveal their different pore size distribution. In the range of relative pressures between 0 and 0.4 differences on the porous texture can be observed. The highest initial N<sub>2</sub> uptake shown by sample C (Fig. 1b) indicates a high volume of narrow micropores (Sing et al. 1985), and the wide knee reveals a wide micropore size distribution. For sample A the narrow knee suggests a narrow micropore size distribution. Finally, in the range of relative pressures between 0.4 and 1, the higher

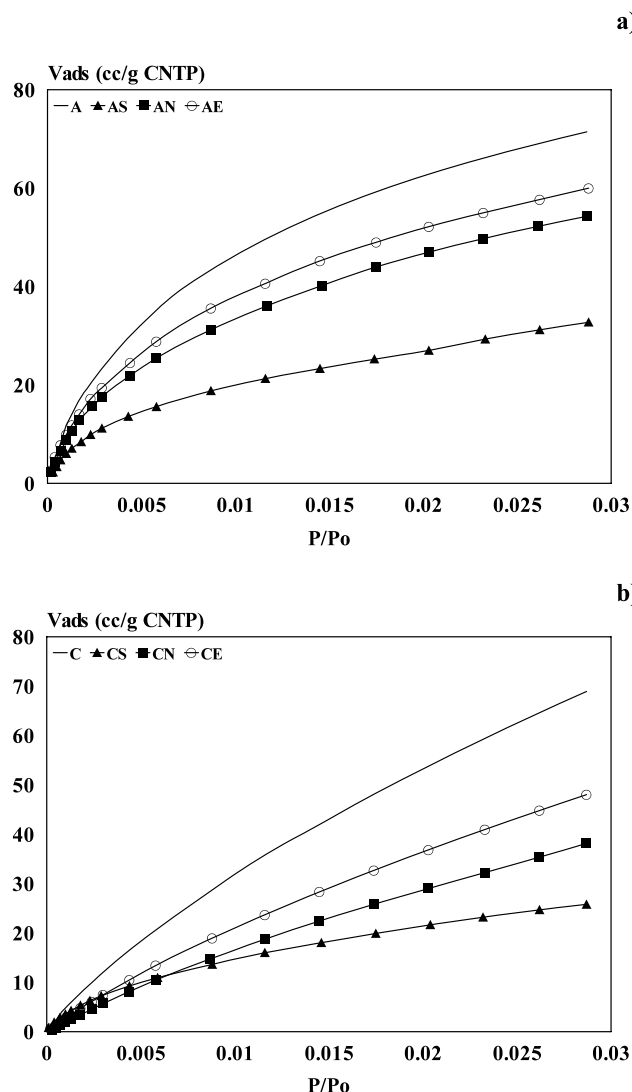


**Fig. 1** Nitrogen gas adsorption isotherms for pyrolysed samples of (a) series A, (b) series C

adsorption capacity shown by sample C is due to its larger mesopore volume.

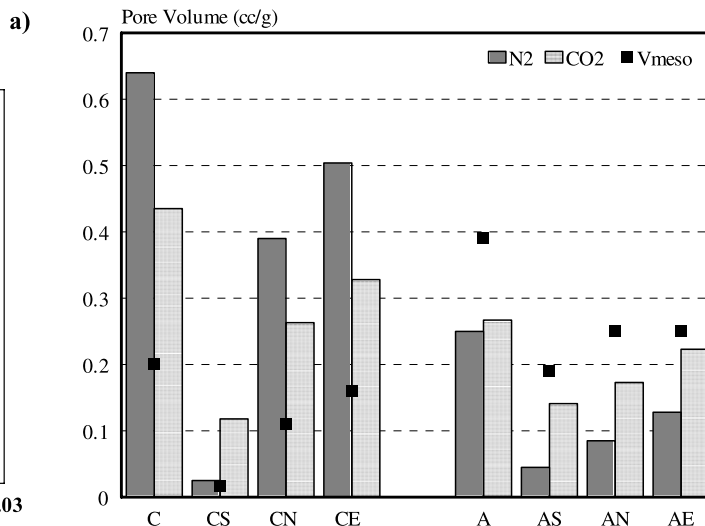
Figures 1 and 2 point out that the impregnation and pyrolysis of the two AC produces a decrease in their adsorption capacities as consequence due to a the partial blockage of the porosity by a fraction of the organic compound. This blockage seems to affect all pore sizes range because the shape of N<sub>2</sub> isotherm is not appreciable changed and, also, a similar decrease in the N<sub>2</sub> and CO<sub>2</sub> adsorption capacity is observed.

Figure 3 compares the volumes of narrow micropore (VCO<sub>2</sub>), total micropore volume (VN<sub>2</sub>) and mesopore volume for high-pressure pyrolysed samples. The differences on the porous texture shown by pyrolysed samples depend on the organic compounds used: sucrose is the most effective for pore blocking, followed by nonane and, finally, ethylene glycol is the less effective one. The largest decrease observed for sucrose is probably related to solid soft during the



**Fig. 2** CO<sub>2</sub> gas adsorption isotherms for pyrolysed samples of (a) series A, (b) series C

heat treatment (mp. 460 K) and to the more efficient pores covering during the pyrolysis. On the other hand, during the heat treatment until 673 K, the nonane and ethylene glycol, both liquids with boiling points of 423 K and 472 K, could be released. The differences observed between n-nonane and ethylene glycol seem to be due to the higher fraction of n-nonane presents in the microporosity (Gregg and Sing 1967; Linares-Solano et al. 1984). The porous texture characterization of the pyrolysed samples obtained at atmospheric pressure (not shown) reveals that nonane and ethylene glycol scarcely modify the AC porosity, meanwhile sucrose produces appreciable changes on porosity. So, the use of sucrose does not require high pressures (the small effect that pressure shows on the pyrolysis of sucrose was previously described by other authors, Inagaki et al. (1981), nor high temperatures).



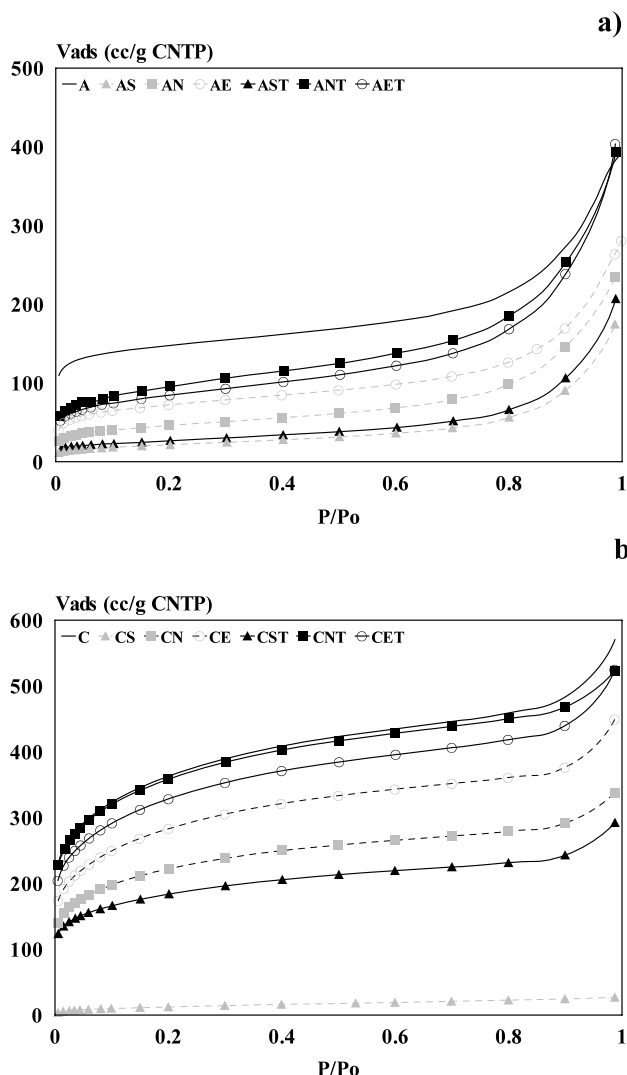
**Fig. 3** Pore volume of narrow microporosity (VCO<sub>2</sub>), total microporosity (VN<sub>2</sub>), and mesoporosity of the AC (A and C) and their pyrolysed samples

The influence of the porosity on the pore blocking can also be observed in Fig. 3 and also depends on the organic compound. For sucrose, the raw AC porosity seems not affect the range of pore size which is being blocked, while for nonane and ethylene glycol it has to be taken into account. Thus, for sample C, with a wide microporosity (VN<sub>2</sub> > VCO<sub>2</sub>), the decrease in both type of pore size is similar and, for sample A, with a narrow microporosity (VN<sub>2</sub> < VCO<sub>2</sub>), a larger decrease in the wide microporosity is observed. Moreover, sample A shows a lower reduction in the mesoporosity.

### 3.2 Heat treatment of pyrolysed samples

#### 3.2.1 Porous texture characterization of carbonized samples

Figure 4 compares the N<sub>2</sub> adsorption isotherms for carbonized and for pyrolysed samples. All samples, except sample AS, show an increase of the adsorption capacity after carbonization due to pore opening. For C series the pore opening is most effective and affects to the whole range of pore size. In the case of sample CNT and CET (Fig. 4b) all carbonaceous deposits have to be removed because the isotherms are identical to that of the raw AC (C). However, for A series, the increase of the adsorption capacity in the range of relative pressures between 0.4 and 1 indicates that pore opening only affects to the mesoporosity (the change in the isotherms at low relative pressure indicates a scarce opening of the narrow microporosity). By comparing results for the three organic compounds, a different behaviour is observed for sucrose for which a significant pore blocking persists. These results contrast with those published by other

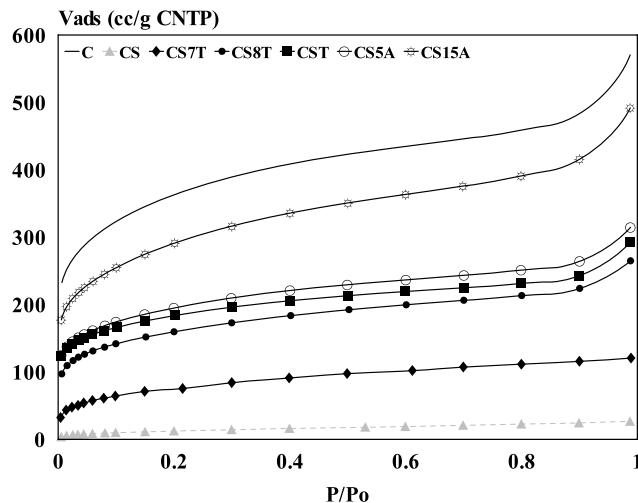


**Fig. 4** Nitrogen gas adsorption isotherms for pyrolysed and carbonised samples of (a) series A, (b) series C

authors (Hayashi et al. 1996), whose observed that a thermal treatment up to 573 K was very suitable to reduce the pore size of an impregnated AC, but, at higher temperatures, the porosity recovers the original values.

### 3.2.2 Control of porosity opening by heat treatment

The pore opening of CS sample seems to be interesting if it can be controlled by thermal treatment or by gasification. This procedure was previously used by other authors (Hayashi et al. 1996; Py et al. 2003; Verma and Walker 1990; Verma 1991) in order to obtain CMS. To check this point, CS was heat-treated at intermediate temperatures (773 K) and characterized by physical adsorption of gases. The results are shown in Fig. 5. At 773 K (CS8T) the porosity opening reaches a maximum because the weight loss (11%) is similar to that obtained at 1273 K (CST) (15%). This result



**Fig. 5** Nitrogen gas adsorption isotherms of samples obtained from heat treatment or by controlled air gasification

confirms that the temperature (673 K) selected for the preparation of pyrolysed samples is correct. A similar behaviour was reported by K. Miura et al. (1991) for AC impregnated with coal tar pitch and phenol-formaldehyde resin. The authors observed a maximum for pore opening at temperatures around 873 K. The isotherm sharp of the sample obtained at 723 K (CS7T) (50 K above the preparation temperature) (shown in Fig. 5) indicates that the pore opening affects, mainly, to the narrow microporosity. This is an interesting result because allows the control of porosity opening by a control of the heat treatment temperature.

The pore opening of the CS sample was carried out, also, by means of a controlled air gasification of the carbonaceous deposits. Air was selected because the high oxygen reactivity towards carbon gasification (Verma and Walker 1990) allows to carry out the gasification at low temperatures. Sample CS was oxidized in air at 673 K during 5 minutes (CS5A) and 15 minutes (sample CS15A) achieving burn-offs of 12% and 30% by weight, respectively. The isotherm of CS5A and CS15A were included in Fig. 5. The isotherm of CS15A reveals a higher adsorption capacity than CST, which is close to that of the C sample indicating that the burn-off produces the removal of carbon deposit and, as consequence, most of the initial porosity was open. In the case of CS5A, the isotherm is similar to that of the CST.

These above described results show that a similar pore opening is obtained by partial air gasification and by the pyrolysis, but lower temperatures and time are required when partial air gasification is used. It has to be point out that, the pore opening can be controlled by selecting the temperature, time and thermal treatment atmosphere.



### 3.3 Study of application as CMS

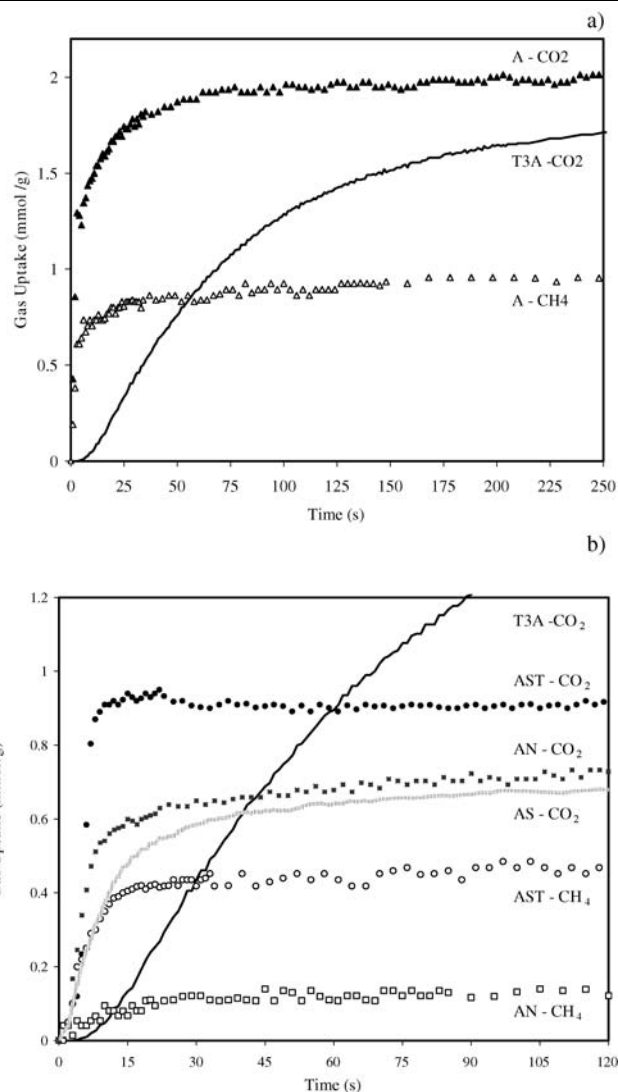
The general objective of the present work is to analyze the effect of pressure and the organic precursor on the AC pore modification. Nevertheless, considering the application of these materials, the study of molecular sieve properties of samples seem to be interesting to determine their future use.

The pyrolysis treatment produces ACs with a narrow microporosity (Fig. 3), specially in samples of series A, which show higher micropore volumes for CO<sub>2</sub> than for N<sub>2</sub> adsorption. The presence of narrow micropores causes a kinetic restriction to the entrance of N<sub>2</sub>, due to the low temperatures at which the adsorption of this gas is performed (Cazorla-Amorós et al. 1996; Gregg and Sing 1967; Rodríguez-Reinoso and Linares-Solano 1988). The presence of this type of porosity makes these materials very useful for gas separation and/or as catalyst supports.

The molecular sieve properties of series A samples have been compared with that of a commercial CMS (Takeda 3A-T3A) in terms of the CH<sub>4</sub> and CO<sub>2</sub> adsorption kinetics (de la Casa-Lillo et al. 1998) (kinetic diameter 0.38 and 0.33 nm, respectively) (Fig. 6). As expected, T3A adsorbs CO<sub>2</sub> while the adsorption of CH<sub>4</sub> is absent in the period of time analysed. For sample A, it can be observed in Fig. 6a, a high adsorption kinetics for both gases due to its porosity (VN<sub>2</sub> ≈ VCO<sub>2</sub>).

The kinetic curves of samples AS, AST, AN and the commercial T3A are shown in Fig. 6b. AS shows the best separation properties because CH<sub>4</sub> is not adsorbed while a considerable and fast CO<sub>2</sub> adsorption is featured. However, due to the decrease in pore volume, the adsorption capacity of CO<sub>2</sub> is lower than that of the original sample A. Sample AN, with higher micropore volume, shows a small increase in the rate of CO<sub>2</sub> adsorption respect to AS and, also, a slight increase in the CO<sub>2</sub> adsorption capacity. However, AN displays CH<sub>4</sub> adsorption capacity as consequence of its larger pore size. Thus, in order to obtain a higher adsorption capacity it is necessary to open the porosity. An example is AST which presents a faster kinetics and larger CO<sub>2</sub> adsorption capacity than AS. Nevertheless, the carbonization process produces an excessive opening in the porosity (high adsorption of N<sub>2</sub> is observed in Fig. 4), increasing the adsorption of CH<sub>4</sub> and suppressing the molecular sieve properties (Fig. 6).

T3A shows typical desirable molecular sieve properties, since it does not retain CH<sub>4</sub> (in the range of time analysed) and it also presents a large CO<sub>2</sub> adsorption capacity. However, faster initial CO<sub>2</sub> adsorption is of a great interest for the application in Pressure Swing Adsorption (PSA) (Yang 1997). In this process, from the economical point of view, it is more interesting that the adsorption stage is accomplished in a short time (40–60 secs) (Pan et al. 1989). In that time range, the capacities of AS and AN are suitable and comparable to that of the commercial CMS. So, considering the



**Fig. 6** Kinetics of adsorption of CO<sub>2</sub> and CH<sub>4</sub> for the commercial CMS (T3A) the AC A (a), and modified samples (b)

simplicity of the preparation of these materials as well as the low cost and the low environmental impact, they are very promising for PSA applications. However, this is a preliminary study and the molecular sieving properties of these materials must be improved by optimization of other process parameters (temperature, time and pressure).

## 4 Conclusions

The results discussed in this paper allows to conclude that:

- High-pressure pyrolysis is beneficial for organic compounds that volatilize during the preparation.
- Sucrose is the most effective for pore blocking, followed by nonane and ethylene glycol.
- Low pyrolysis temperature is interesting because allows a tight control of pore opening by heat treatment or by

controlled gasification. The pore opening depends both on the organic compound and on the ACs.

- For organic liquid compounds, the high-pressure pyrolysis process using pressure is an interesting approach to prepare CMS for CO<sub>2</sub>/CH<sub>4</sub> separation.

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