

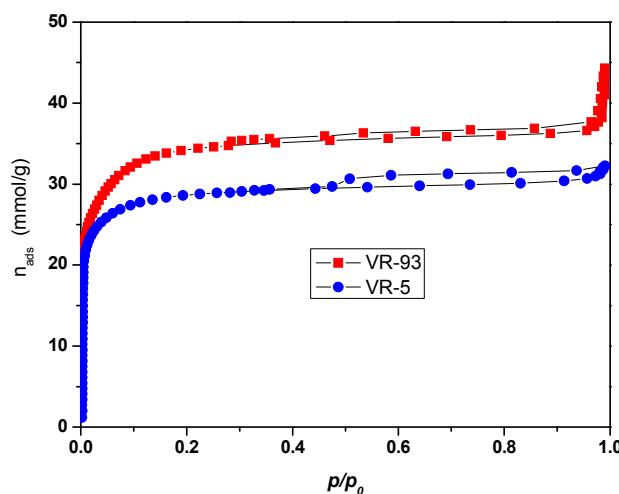
Supporting Information

*Preparation of the carbon molecular sieves*

Two different petroleum pitches were obtained by pyrolysis of a vacuum residue under inert atmosphere, at two different conditions: 693 K for 3 hours, to yield an almost isotropic pitch (with only 5% of mesophase, pitch VR-5), and 733 K for 1.5 hours, yielding a mesophase pitch (with a high mesophase content, 93%, pitch VR-93). During the pyrolysis process, molecules constituent of the petroleum residue increase in aromaticity and size by condensation and polymerization reactions, this giving rise to the formation of large polycyclic aromatic hydrocarbons (PAHs). These PAHs pile-up forming a liquid crystal phase called carbon mesophase.<sup>1</sup> After the pyrolysis process, the pitches were mixed with KOH in a ball mill, in a KOH/pitch ratio of 3/1, for 30 minutes. Activation of the pitch was carried out by treating the KOH/pitch mixture at 1073 K for 2 hours under inert atmosphere, to obtain activated carbon molecular sieves VR-5 and VR-93. The mixtures were activated either in monolith and powder shape. Monoliths were prepared by uniaxial pressing of the mixtures at 400 MPa and room temperature. The addition of a binder is not necessary as the own pitch has binding properties. Finally, the carbon molecular sieves were washed, first with a HCl solution (10 wt%) and finally with distilled water.

*Textural characterization of the carbon molecular sieves*

The textural characterization of the carbon molecular sieves was performed by gas adsorption at cryogenic temperatures and immersion calorimetry measurements into liquids of different molecular dimensions. N<sub>2</sub> adsorption-desorption measurements were performed in a home-made manometric equipment up to atmospheric pressure (relative pressure  $p/p_0$  of 1). Prior to the adsorption measurements, samples were degassed at 523 K for 4 h. Fig. S1 shows the nitrogen adsorption-desorption isotherms for the VR-5 and VR-93 carbon molecular sieves.



**Fig. S1.** N<sub>2</sub> adsorption-desorption isotherms at 77 K for the VR-5 and VR-93 carbon molecular sieves.

As it can be observed in Fig. S1, both samples exhibit a type I isotherm characteristic of microporous solids. The modification of the preparation conditions gives rise to an increase in the amount of nitrogen adsorbed with the mesophase content, i.e. a higher development of porosity for sample VR-93, together with a widening of the micropore size distribution, i.e. a wide knee in the nitrogen isotherm at low relative pressures.

Application of the BET equation to the nitrogen adsorption data allows estimating the “apparent” surface area while the application of the Dubinin-Radushkevich equation allows determining the total micropore volume ( $V_t$ ). Table 1 reports the textural parameters obtained from the nitrogen adsorption data.

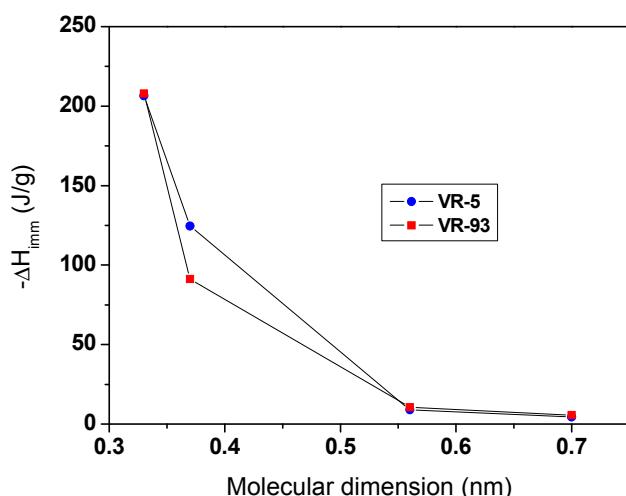
**Table 1.** Textural parameters obtained from the N<sub>2</sub> adsorption data at 77 K.

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>o</sub> (cm <sup>3</sup> /g)	V <sub>t</sub> (cm <sup>3</sup> /g)
VR-5	2450	1.03	1.12
VR-93	2895	1.06	1.42

B.E.T. surface area for the synthesized carbon molecular sieves achieves a value as high as  $2895\text{ m}^2/\text{g}$  for the sample with the maximum mesophase content. Additionally, these samples are characterized by an extremely high total pore volume, mainly in the micropore range.

A further characterization of the porous structure was performed by immersion calorimetry into liquids of different molecular dimensions, i.e. dichloromethane (0.33 nm), benzene (0.37 nm), 2,2-dimethylbutane (0.53 nm) and  $\alpha$ -pinene (0.7 nm). Calorimetric measurements were performed in a Setaram Tian-Calvet C80D calorimeter working at 303 K. Before the experiment, the samples were degassed at 423 K for 4 h in a glass bulb connected to the vacuum equipment. After sealing the sample under vacuum, the glass bulb was introduced into the calorimetric chamber together with the immersion liquid. After thermal equilibrium was reached, the sample tip was broken and the sample was allowed to interact with the corresponding liquid. The heat evolved during this process ( $-\Delta H_{imm}$ ) was recorded as a function of time. Calorimetric measurements were repeated three times with a final experimental error below 3–4%.

Fig. S2 shows the enthalpy of immersion for the different carbon molecular sieves into liquids of different molecular dimensions.



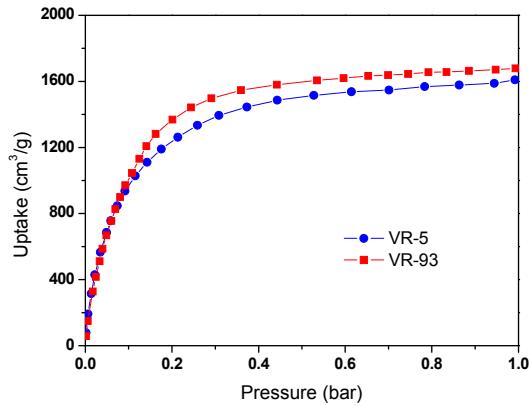
**Fig. S2.** Enthalpy of immersion (J/g) into different molecules for the different carbon molecular sieves; dichloromethane (0.33 nm), benzene (0.37 nm), 2,2-dimethyl-butane (0.53 nm) and  $\alpha$ -pinene (0.7 nm).

In the absence of specific interaction at the solid-liquid interface, immersion calorimetry into liquid of different molecular dimensions can be used to estimate the total surface accessible for a given molecule. As it can be observed in Fig. S2, a small molecule such as dichloromethane, with a kinetic diameter of 0.33 nm (similar to nitrogen; 0.36 nm) is able to access the whole porosity on both samples (VR-5 and VR-93), giving rise to a large enthalpy value (~ 208 J/g). However, a molecule with a slightly higher diameter, such as benzene, exhibits important restrictions, i.e. there is a sudden decrease in the heat of interaction, these effects being more drastic for the VR-93 sample. Finally, 2,2-dimethyl-butane and  $\alpha$ -pinene, with a kinetic diameter of 0.56 nm and 0.70 nm, respectively, are unable to access the porous structure in both samples. These results constitute an empirical prove of the molecular sieve effect on these activated carbon materials. According to the calorimetric measurements, the pore size opening on both samples must be below 0.56 nm, this value being slightly lower for sample VR-93, i.e. narrower micropore entrance on this sample compared to VR-5.

In summary, textural characterization results show that activated carbon monoliths prepared from mesophase pitch and using KOH as activating agent exhibit a highly developed porosity, mainly in the microporous range, together with an extremely large accessible surface area and a well-defined pore size entrance (below 0.56 nm).

#### *CO<sub>2</sub> adsorption isotherms at 195 K*

CO<sub>2</sub> adsorption isotherms at atmospheric or high pressure were measured in a home-made manometric equipment. In order to certify the excellent adsorption behaviour of synthesized carbon molecular sieves, the CO<sub>2</sub> adsorption capacity was measured at 195 K. As it can be observed in Fig. S3, the total adsorption capacity at 195 K and atmospheric pressure is extremely large for both samples with a maximum amount adsorbed of ~1600–1700 cm<sup>3</sup>/g. Consequently, even at low temperatures (195 K), where kinetic restrictions for CO<sub>2</sub> could be expected on carbon molecular sieves with a narrow pore size opening (pore size below 0.56 nm), both samples exhibit an extremely large adsorption capacity. These results corroborate the excellent adsorption behaviour reported above for VR-5 and VR-93 carbon molecular sieve monoliths at high pressure (50 bar) and room temperature (298 K). Interestingly, while at 298 K and atmospheric pressure the CO<sub>2</sub> adsorption isotherm was mainly linear with pressure, at low temperature (195 K) and atmospheric pressure the adsorption isotherm exhibits a type I shape, i.e. there is a narrow knee in the amount adsorbed at low pressures, which reflects the effect of the adsorption temperature in the adsorption process. Physical adsorption is an exothermic process in such a way that a decrease in the adsorption temperature produces an increase in the amount adsorbed together with a shift to lower absolute pressures in the filling of the micropores (at 195 K the saturation pressure (P<sub>0</sub>) for CO<sub>2</sub> is lower compared to room temperature and, consequently, at a given absolute pressure (P), the relative pressure (P/P<sub>0</sub>) is higher, thus explaining the preferential filling of the micropores at low absolute pressure when the adsorption isotherm is performed at 195 K).



**Fig. S3.** CO<sub>2</sub> excess adsorption isotherms at 195 K and atmospheric pressure for samples VR-5 and VR-93.

#### References

- 1 H. Marsh, M. Martínez-Escandell, F. Rodríguez-Reinoso, *Carbon*, 1999, **37**, 363-390.
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