

STRATEGIES FOR THE OPTIMIZATION OF NANOPOROUS ADSORBENTS FOR METHANE STORAGE

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ABSTRACT: Nanoporous adsorbents for methane storage should not only contain a high volume of micropores with a certain size (0.8- 1.12nm) but a sufficiently high bulk density to maximize the amount of gas stored in a minimum volume of container. Unfortunately, these materials contain inevitably some mesoporosity and interparticle spaces where methane gas is stored with lower density. Here, three possible strategies to maximize the use of porosity of a carbonaceous adsorbent obtained from mesophase pitch are described. The first one suggests the use of precursors with high mesophase content, which allows obtaining the best micropores/bulk density ratio. The second strategy consists in the formation of methane hydrates in a mesoporous carbon. Finally, the growing of MOF in the presence of activated carbon monolith that allows a synergy between the two components is proposed.

KEYWORDS: activated carbon, methane adsorption; MOF/C composites; methane hydrate

1. INTRODUCTION

Natural gas, and methane as its main component, is gaining increasing interest from governments because it is a cheaper and much cleaner alternative than conventional fuels used in the automotive industry.

The main drawback with using methane is its low energy density. Consequently, it is necessary to use specific technologies that allow storing the maximum amount of gas in the minimum volume of container to be competitive in the market. Compression of natural gas in stainless steel cylinders has been the most widely used technology for many years. The development of nanoporous adsorbents is an alternative to compression as it allows decreasing the pressure from 200 bar to less dangerous levels of 35-50 bar and thus design containers more adaptable to dead space of the car without compromising the autonomy of the vehicle.

Activated carbon is a material with unique characteristics in terms of stability and recyclability (Silvestre-Albero, 2011). There are numerous studies about the synthesis and design of the porosity of these materials to maximize the density of adsorbed methane (Menon, 1998). In

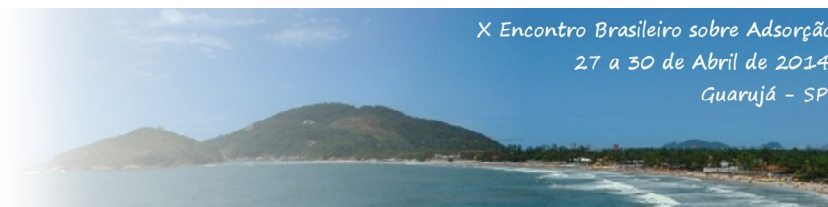
this work, the challenge of maximizing volumetric methane capabilities of activated carbons prepared from petroleum residue is approached by implementing new strategies not only for an optimum use of the micropores, but also to take advantage of the mesopores and interparticle spaces where methane is stored with a lower density. The strategies described throughout this work are:

- a. Increased bulk density by increasing mesophase content.
- b. Methane hydrate formation on wet mesoporous carbons.
- c. In-situ growth of MOFs in the pores of activated carbon.

2. MATERIALS AND METHODS

In this work, activated carbons were prepared from mesophase pitches by the pyrolysis of different petroleum residues and subsequent chemical activation with KOH at 800°C. Their characteristics are summarized in Table 1.

LMA741 and LMA742 samples were prepared using the same petroleum residue but a different heat treatment so as to produce two pitches with very different mesophase content (0



and 100%, respectively). Sample LMA726 was selected to be wetted with distilled water to a RW = 1.8 (mass of water per mass of dry material) and make methane adsorption on the wet carbon. LMA74 sample (in monolith shape) was used as matrix for growing MOF in the pores. The hybrid material was called MOF/C.

Table 1. Characteristics of activated carbons.

Sample	%mesophase	KOH:precursor
LMA741	10	3:1
LMA742	100	3:1
LMA726	93	6:1
LMA74	93	3:1

All samples were characterized by N₂ adsorption at 77 K in a volumetric equipment designed and built at the Laboratorio de Materiales Avanzados, now commercialized under the name N2G-sorb-G (Gas to Materials Technologies (www.g2mtech.com)). Methane Adsorption was performed on a high pressure volumetric equipment also designed and built by our laboratory, now commercialized as iSorbHP by Quantachrome Corporation. Methane adsorption was performed at 25 ° C to 50 bar at most samples. Degasification of the samples was carried out at 250 ° C during 4 hours. In the case of the wet sample, LMA726, methane adsorption was carried out at 2° C up to 100 bar, prior degassing at -20 ° C to avoid loss of water.

Transmission electron microscopy (TEM) analyses were performed on a JEOL JEM-2100F microscope. Scanning Electron Microscopy (SEM) analyses were performed on a HITACHI-SU8030 microscope.

X-ray powder diffraction (XRD) was carried out in a RIGAKU ATXG diffractometer Equipped with a 18kW Cu rotating anode, a MLO nanochromator and a high-count-rate scintillation detector (measurements carried out over a range of 5°<2θ<20° in 0.05° step width to 2 °/min scanning speed.

3. RESULTS AND DISCUSSION

In order to optimize the use of a nanoporous material for methane storage, several factors should be considered. The most important are the fact that microporosity must be adequate (0.8-1.12 nm) to achieve optimal packing gas but also that bulk density should be sufficiently high so that the storage per unit volume is maximized. These two factors are difficult to get together, but it is possible to reach a good compromise by controlling the carbon precursor. Additionally, new alternative strategies are emerging based on the use of the larger porosity (large micropores and narrow mesopores), which in principle is not suitable for methane adsorption.

3.1. Effect of mesophase content

Petroleum residues have shown to be a rather versatile material for designing the porosity of an activated carbon (Hull, 2014). This versatility derives from the fact that controlling the composition of the petroleum residue and the pyrolysis conditions (temperature, residence time, pressure), it is possible to produce pitches with different characteristics. These variables affect the subsequent chemical activation process with KOH and the final density of the activated carbon (Monteiro de Castro, 2010). Two pitches coming from the same petroleum residue have been prepared, having 100 % and 10% mesophase content (LMA742 and LMA741, respectively), which were activated with KOH in similar conditions (Table 1). As observed in Table 2, sample LMA742 contains a larger micropore volume than LMA741 sample (1.07 versus 0.94 cm³/g). One would expect that the bulk density may be lower in this sample; however, density is slightly higher (0.54 and 0.53 g/cm³, respectively). Figure 1 show TEM images for the two activated carbons. It seems that the sample coming from the pitch with the highest mesophase content (LMA742) apparently has a more compact carbonaceous skeleton. This is possible because the mesophase of this pitch is more ordered, and apparently it seems that a more ordered structure remains after chemical activation, resulting in a more dense activated carbon (Marshall and Reinoso, 2006).

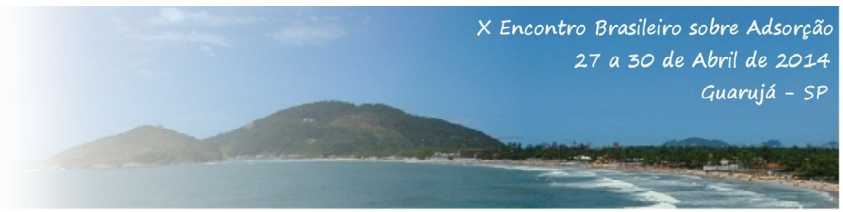


Table 2. Specific surface area calculated by the BET equation, micropore volume calculated by the Dubinin-Radushkevich equation and total pore volume obtained at $P/P_0 = 0.95$ from the N_2 isotherms.

Sample	S_{BET} m^2/g	V_{micro} cm^3/g	V_{total} cm^3/g	Bulk density g/cm^3
LMA741	2650	0.94	1.30	0.53
LMA742	3000	1.07	1.43	0.54
LMA74	2120	0.89	0.94	0.49
LMA726	3670	1.20	2.40	0.54

Therefore, it was possible to increase the density of the material and create a large amount of microporosity using mesophase pitches with high mesophase content. The result of methane storage values obtained are near 169 and 179 V/V at 50 bar and 25°C for LMA742 and LMA741, respectively.

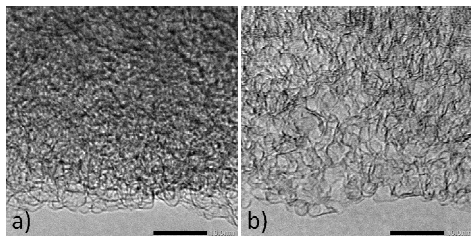


Figure 1. TEM images for activated carbons with (a) low-mesophase (LMA741) and (b) high mesophase content (LMA742).

3.2. Methane hydrates formation

Another possibility for increasing methane storage capacity of the activated carbon is to add a certain amount of water in the pores to form stable structures of ice between methane and water called methane clathrates (or hydrate). These compounds are formed naturally in the ocean at low temperatures and high pressures. It has been discovered that there are reserves of methane hydrates in the oceans that exceed twice those of other fossil fuels. However, their extraction from the oceans is still under study due to the risks that may occur when releasing such gaseous masses from the seabed. However, since a volume of clathrate can release up to 180 volumes (STP) of methane (Sloan, 1998), scientists believe that the

synthetic methane hydrates can be a viable way to store and transport methane at lower cost and also safer than the current technologies (liquefaction, compression).

In this work a mesoporous carbon with high surface area ($3670 m^2/g$), LMA726, was selected to be moisten with water up to saturation ($R_w = 1.8$). The adsorption of methane on the dry and wet sample at 2°C to 10 MPa was measured. Figure 2 shows the results of methane storage of the wet and dry carbon in gravimetric basis. It can be observed that the wet carbon has almost no adsorption of methane below 5 MPa, as it seems that water is blocking the porosity. However, above 6 MPa methane adsorption begins with a sigmoidal curve, reaching uptakes of up to 50 wt%. This value is much larger than that of the dry carbon, 30 wt%. This behavior could indicate the formation of methane hydrates in the pores of the activated carbon. The hysteresis cycle closing at a lower pressure (near to 3 MPa) is another indication of the possible formation of methane hydrates, since its decomposition in free water should occur at 3.5 MPa at 2°C, according to the water+methane phase diagram.

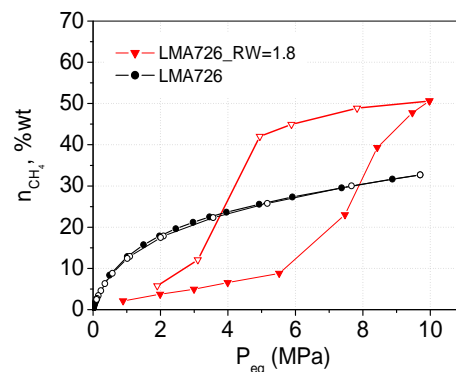


Figure 2. Methane adsorption isotherm for dry and wetted LMA726 at 2°C up to 10 MPa.

This strategy is novel because it allows using the interparticle space, macro and mesopores by hydrate formation, while in narrow pores there is still free methane adsorbed. Both processes are added to increase the adsorption capacities of the material. However, its practical application is still limited because the kinetics of hydrate formation is extremely slow. Understanding the mechanism of hydrate formation in an activated carbon is still in discussion in the scientific community.



3.3. MOF growth in the presence of activated carbon.

While activated carbons are excellent adsorbents for gases, metal-organic hybrid materials known as MOFs are increasingly drawing attention as they have demonstrated one of the largest capacities for methane adsorption reported so far (Peng, 2013). This is possible mainly because these materials can be designed with a single pore size. However, their practical application is still limited due to its low thermal, mechanical and chemical stability. The preparation of composite materials, MOF/C, aims to achieve a synergy between the two components minimizing the shortcomings that have each one individually. To implement this idea, in this work an activated carbon monolith (LMA74) was selected to grow a MOF material on its surface.

The crystallinity of MOF in the composite was analysed by X-ray powder diffraction (XRD). The results in Figure 3 (a) show that the MOF in the composite are isostructural with the original MOF, indicating that the activated carbon does not affect to the MOF's growth. An excellent MOF/activated carbon interface was confirmed by using scanning electron microscopy (SEM). SEM images (Figure 3 (b)) also show that the crystal size depends on the activated carbon pore diameter since the growing begins inside the carbon pore.

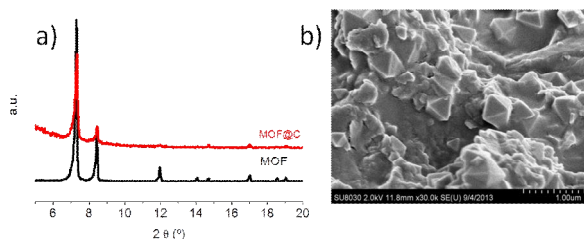


Figure 3. (a) X-ray pattern for the original MOF and the monolith. (b) Growth of MOF crystals in the presence of the monolith.

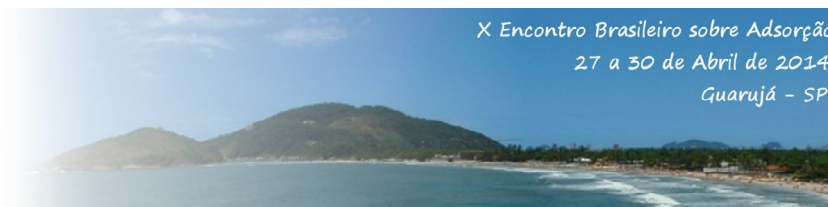
Despite the expectations for these hybrid materials, there are still some problems to solve as the low thermal conductivity of MOFs materials and activated carbon materials. This parameter is important because methane adsorption is an exothermic process that must be controlled to avoid temperature fluctuations during cycles of uploading and discharge.

4. CONCLUSIONS

The use of mesophase pitches of high mesophase content allowed to reach a good compromise between micropore volume and bulk density, leading to methane adsorption capacity on volumetric basis proximate to 180 V / V at 50 bar pressure and room temperature. On the other hand, the addition of a certain amount of water to the activated carbon is one of the most promising methods to achieve a high methane storage capacities (50% wt in this work) strategies, using not only the micropores but also the interparticle space through the formation of stable inclusion structures between water and methane, known as methane hydrates. Finally, the growth of a MOF in the presence of activated carbon was presented, obtaining hybrid materials with good carbon/MOF interface, without affecting the crystallinity of the MOF.

5. REFERENCES

- CASCO M.C., MARTÍNEZ-ESCANDELL M., SILVESTRE-ALBERO J., RODRÍGUEZ-REINOSO F. Effect of the porous structure in carbon materials for CO₂ capture at atmospheric and high-pressure. *Carbon*. v 67, p. 230-235, 2014.
- MARSH H. AND RODRÍGUEZ-REINOSO F. *carbon*. Elsevier, 2006.
- MENON V.C., KOMARNEMI S. Porous adsorbents for vehicular natural gas storage: a review. *Journal of porous materials*. v. 5, p. 43-58, 1998
- MONTEIRO DE CASTRO M.C., MARTÍNEZ-ESCANDELL M., RODRIGUEZ-REINOSO F. Hydrogen adsorption on KOH activated carbons from mesophase pitch containing Si, B, Ti or Fe. *Carbon*. v. 48, p. 636-644, 2010.
- SILVESTRE-ALBERO J., WAHBY A., SEPÚLVEDA-ESCRIBANO A., MARTÍNEZ-ESCANDELL M., KANEKO K., RODRÍGUEZ-REINOSO F. Ultrahigh CO₂ adsorption capacity on carbon molecular sieves at room temperature. *Chem. Commun*. v. 47, p. 6840-6842, 2011.



SLOAN, E.D., KOH C., Clathrate hydrate of natural gas, Third Edition. *Marcel Dekker, New York*, 1998.

PENG Y., KRUNGLEVICIUTE V., ERYAZICI I., HUPP J., FARHA O.K., YILDIRIM T. Methane storage in metal-organic framework: current records, surprise findings, and challenges. *J. Am. Chem. Soc.*, v. 32, p.11887-11894, 2013.

6.ACKNOWLEDGMENTS

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