ORDERED NANOSTRUCTURED CARBONS USED AS MATERIALS FOR HYDROGEN STORAGE.

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Introduction

The need for an hydrogen storage which could be suitable for transportation applications has led to an important research activity and several technologies have been proposed [1]. Physical adsorption has received much attention because of its high energy efficiency; but due to the very low boiling point of hydrogen, a low temperature is required to achieve a high energy density so that the global energy efficiency is reduced. Nevertheless, this technology has the advantage that the desorption process can be easily controlled by temperature and pressure variations.

Numerous experimental studies have been done to test different solids such as activated carbons [3,4], nanotubes and nanofibers [5,6]. For carbonaceous materials, most studies which have been done at room temperature lead to values below 1 wt%, while the adsorption capacities at 77 K are of the order of few percents. In order to be suitable for transportation applications, it is estimated that the density in the storage system should be at least 6.5 wt% [1,2].

Either experimental or theoretical studies have shown that the presence of micropores was one of the key parameters which influences the hydrogen adsorption capacity. Several activation processes have been developed to modify carbon material porous structure, but the pore size distribution of activated carbons is generally wide. In this context, the possibility to synthetize ordered porous carbons by replication from silica templates is of great interest. The carbon materials obtained with this procedure have numerous interesting properties [8-10]:

- a microporous volume which can be high,
- a very well defined and controlable micro-structure,

- the presence of a three dimensional mesoporous network which enhance the dynamics of diffusion in the material,
- the possibility to modify the microporous and mesoporous textures by changing the silica template and the carbon precursor.

The aim of this study was to determine the capacity of hydrogen adsorption at 77 K of synthetized ordered mesoporous carbon materials with different structural and textural properties.

Experimental

The synthesis of ordered mesoporous carbons from silica templates has already been described in previous papers [8-11]. It can be summarized as follow: a carbon precursor is inserted in the porosity of a silica material by a gas or liquid process followed by a carbonization when necessary. The silica template is then removed through an HF treatment. The samples tested in this study were prepared from two mesoporous silica templates, SBA-15 and MCM-48. Two different impregnation ways were used: chemical vapor deposition of propylene, and liquid phase impregnation of sucrose and pitch.

The carbon materials were characterized using nitrogen and carbon dioxide adsorption. This last method is useful to obtain information on the microporosity of solids. N_2 adsorption isotherm at 77 K was used to determine the total surface area (TSA) with the BET method, the total porous volume V_p at $P/P_0 = 0.95$, and the microporous volume V_{N2} with Dubinin-Radushkevich equation. The microporous volume V_{CO2} was computed from the CO_2 adsorption isotherm at 273 K with Dubinin-Radushkevich equation. The main characteristics of the samples are presented in table 1.

Sample	Silica template	Carbon precursor	TSA (m^2/g)	V_p (cm^3/g)	V_{N2} (cm^3/g)	V_{CO2} (cm^3/g)
CB15	SBA-15	Pitch	754	0.50	0.23	0.26
CS15	SBA-15	Sucrose	1200	0.90	0.41	0.27
CPr15	SBA-15	Propylene	711	0.76	0.20	0.09
CS48	MCM-48	Sucrose	2390	1.22	0.68	0.36
CB48	MCM-48	Pitch	1130	0.64	0.33	0.18

Table 1: Characteristics of the carbon materials.

The hydrogen adsorption capacity was measured with a volumetric apparatus. 1 g of carbon sample was put in a 20 cm^3 cell, it was then outgassed under vacuum at 573 K. The sample cell was then immersed in a dewar filled with liquid nitrogen to reach 77 K.

The hydrogen adsorption capacity was computed from the amount of gas which desorbed from the material.

Results and Discussion

As already mentioned, the characteristics of the carbon materials depend on the nature of the carbon precursor and template. The presence of a significant microporous volume suggested by the N_2 adsorption isotherms has been confirmed by the CO_2 adsorption measurements. The use of sucrose as a carbon precursor leads to highly microporous carbon materials. This microporosity results not only from the dissolution of the silica template, but also from the sucrose carbonization.
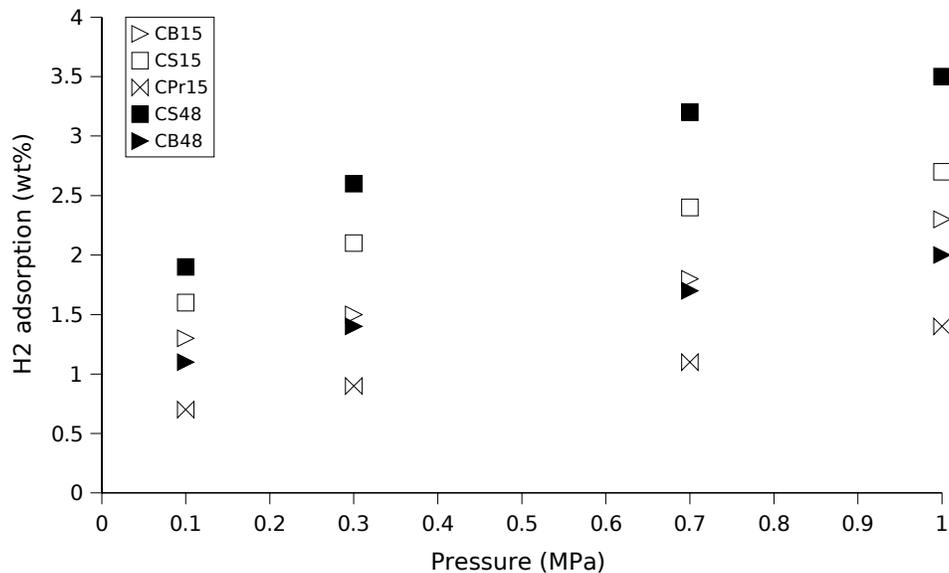

Figure 1: Hydrogen adsorption capacity of carbon materials at 77 K.

The measured adsorption capacities at 77 K are presented in Figure 1. The adsorption capacities range between 1.3 and 3.5 wt% at 1 MPa. From these results, it can be clearly seen that the synthesis method of the carbon has a great influence on the quantity of hydrogen adsorbed by the material. The lowest values are obtained with carbons obtained by the gas method while materials synthetized with the liquid sucrose solution impregnation leads to the highest. This observation can be done whatever the silica template used to build the replica. As pointed out by other authors on other types of carbon materials, this results confirm the importance of the porous structure of the material. It can be seen that there is a correlation between the microporous volume of the material and its ability to adsorb hydrogen.

Conclusions

It has been shown that ordered mesoporous carbon materials are suitable for the adsorption of hydrogen at 77 K. The physical adsorption of hydrogen on such carbon materials is clearly a process driven by the amount of nanometer sized pores. By changing the silica template and the carbon synthesis process, one should be able to optimize the porous structure of the carbon materials in order to achieve higher hydrogen storage capacities.

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