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The Influence of Microporosity on the Hydrogen Storage Capacity of Ordered Mesoporous Carbons

ROGER GADIOU*
Institut de Chimie des Surfaces et Interfaces, UPR CNRS 9069, 15 rue Jean Starcky,
68057 Mulhouse cedex, France
R.Gadiou@uha.fr

NATHALIE TEXIER-MANDOKI AND THIERRY PIQUERO
CEA Le Ripault, BP 16, 37260 Monts, France

SEIF-EDDINE SAADALLAH
Institut de Chimie des Surfaces et Interfaces, UPR CNRS 9069, 15 rue Jean Starcky,
68057 Mulhouse cedex, France

JULIEN PARMENTIER AND JOËL PATARIN
Laboratoire de Matériaux Minéraux, UMR CNRS 7016, Ecole Nationale Supérieure de Chimie de Mulhouse,
3 rue Alfred Werner, 68093 Mulhouse cedex, France

PATRICK DAVID
CEA Le Ripault, BP 16, 37260 Monts, France

CATHIE VIX-GUTERL
Institut de Chimie des Surfaces et Interfaces, UPR CNRS 9069, 15 rue Jean Starcky,
68057 Mulhouse cedex, France

Abstract. The adsorption of hydrogen on nanostructured carbons prepared by templating of mesoporous silicas has been studied at 77 K and between 0.1 and 1 MPa. The maximum capacity was obtained with a carbon synthetized by a sucrose liquid infiltration process in MCM-48 silica. It was observed that the hydrogen weight percentage which can be adsorbed on a carbon can be correlated to its microporous volume determined by CO_2 adsorption and Dubinin-Radushkevich equation.

Keywords: adsorption, hydrogen, ordered mesoporous carbons

1. Introduction

Several technologies have been proposed for the design of an hydrogen storage device which could be suitable for transportation applications (Schlapbach and Züttel, 2001). Some technologies such as compressed or cryogenic hydrogen lower the global energy efficiency of the process. Storage in metal hydrides such as $LaNi_5$ allow a high volumetric storage density (Züttel, 2003) but the mass storage is low except for light

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*To whom correspondence should be addressed.

weight complex hydrides (Bogdanovich et al., 2000). The other difficulties are that the absorption reaction leads to important thermal effects and that density changes induce important mechanical stress on the material.

Physical adsorption is based on a weak interaction between the solid material and the gaseous hydrogen: between 1 and 10 kJ/mol. It is therefore fully reversible and has a high energy efficiency. Nevertheless, the key point is to obtain a high energy density, that is to store an important amount of gas on the solid. This can only be achieved if the adsorption temperature is not too far from the condensation temperature of the adsorbate. As the boiling point of hydrogen is 20 K, the tank should be cooled and insulated. Nevertheless, the reversibility of the process allow a good control of the desorption process by temperature and pressure variations. The US DOE has stated that the density in the storage system should be at least 6.5 wt% and 62 kg/m^3 in order to be suitable for transportation applications (Schlapbach and Züttel, 2001; Züttel, 2003). Presently, an efficient hydrogen storage medium which reach these goals is not available at room temperature.

During the last two decades, a large number of carbon materials have been studied such as activated carbons (Nijkamp et al., 2001; Zhou and Zhou, 1996, 2004; de la Casa-Lillo et al., 2003), single-wall or multi-wall nanotubes and graphite nanofibers (Chahine and Bose, 1994; Tibbets et al., 2001). The results are widely spread but most studies lead to values below 1 wt% at ambient temperature, while the adsorption capacities at 77 K are of the order of few percents.

From a theoretical point of view, all the modeling studies have confirmed that the maximum hydrogen storage which could be achieve at room temperature is close to 1 wt%. Grand Canonical Monte-Carlo simulations have also shown that the optimum pore size was below 1 nm at room temperature (Rezpka et al., 1998; Lamari-Darkrim et al., 2002). This theoretical result is in good agreement with experimental results obtained on activated carbons (de la Casa-Lillo et al., 2003; Texier-Mandoki et al.). 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 such porous materials, more than 50% of the total porous volume can be constituted of macropores (Quinn and MacDonald, 1992). As adsorption in macropores is only monolayer adsorption, its contribution to the total adsorbed volume of hydrogen is negligible.

During the last five years, several synthesis routes of ordered mesoporous carbons by replication from silica templates have been presented (Ryoo et al., 1999; Vix-Guterl et al., 2002; Vix-Guterl et al., 2003; Parmentier et al., 2004). These materials have numerous properties which may be of interest, such as a microporous volume which can be large and the presence of a three dimensional mesoporous network which enhance the dynamics of diffusion in the material. For the study of hydrogen storage on carbon materials, another advantage is the possibility to vary the microporous and mesoporous texture independently by changing the silica template, the carbon precursor and the synthesis parameters. The aim of this study was to study the influence of the textural properties of nanostructured carbon materials on their capacity to adsorb hydrogen at 77 K.

2. Experimental

2.1. *Materials Studied*

The basis of the synthesis of ordered mesoporous carbons from silica templates has been described previously (Ryoo et al., 1999; Vix-Guterl et al., 2002; Vix-Guterl et al., 2003; Parmentier et al., 2004). A carbon precursor is inserted in the porosity of a silica material by a gas or liquid process, and a carbonization of the carbon/silica mixture is done when necessary. The silica template is then removed with the help of an HF treatment. For this study, the materials tested have been 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 synthesis can be briefly summarized as follow:

CB15 and CB48. The silica was impregnated at 575 K with petroleum pitch 'Ashland A240' during 4 hours. The mixture was then heated under Argon up to 1225 K at 3 K/min to convert the pitch into carbon (Vix-Guterl et al., 2002, 2003; Parmentier et al., 2004).

Table 1. Characteristics of the carbon materials.

Sample	Silica template	Carbon precursor	C in C/SiO_2 (wt%)
CB15	SBA-15	Pitch	36
CS15	SBA-15	Sucrose	37
CPr15	SBA-15	Propylene	40
CS48	MCM-48	Sucrose	37
CB48	MCM-48	Pitch	36

CS15 and CS48. The silica was impregnated with an aqueous solution of sucrose and sulfuric acid (Ryoo et al., 1999). The mixture was then dried and a second impregnation was done. The sucrose/silica composite was then heated at 1173 K under vacuum.

CPr15. Pyrolytic carbon was deposited in the silica template by chemical vapor insertion of propylene at 1020 K. The highest value of carbon which can be inserted with this method is closed to 55 wt% of the carbon/silica composite, which is close to the theoretical value. In this experiment, the synthesis was stopped in order to insert only 40 wt% of carbon in the silica.

The amount of carbon inserted in the silica matrix for the carbon materials are presented in Table 1. N_2 adsorption isotherm at 77 K was determined with a Micromeritics ASAP 2010 apparatus, BET method was used to compute the total surface area (TSA), and the total porous volume V_P was measured at $P/P_0 = 0.95$. The CO_2 adsorption isotherm at 273 K was obtained with a Quantachrome Autosorb A1-MPLP apparatus. The microporous volumes V_{N_2} and V_{CO_2} were determined with Dubinin-Radushkevich equation from the corresponding isotherms.

The N_2 adsorption isotherms of the five samples have a typical shape which shows the presence of micro and mesoporosity for all samples (see Fig. 1). As expected, the pore size distribution in the mesopore range is related to the template which was used for the synthesis. The MCM-48 silica has a mesoporous pore network with a mean pore diameter of 2.6 nm which is typical for this material (Kumar et al., 2001). The wall thickness for this template is close to 1 nm, therefore the presence of micropores with a similar mean diameter is expected for the carbon materials. But as the filling of carbon inside the silica template is not complete, the formation of the porosity in the carbon materials can be divided in two mechanisms (Fuertes et al., 2004).

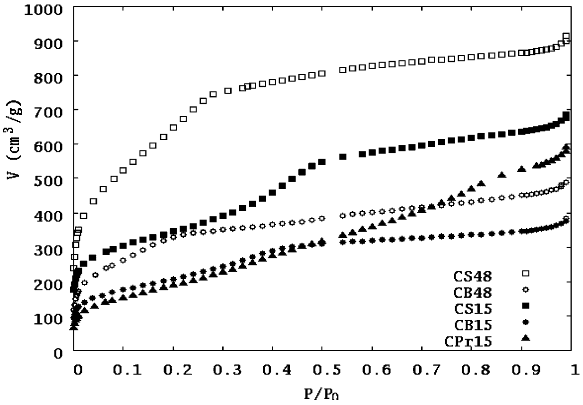

Figure 1. N_2 adsorption isotherms at 77 K for the nanostructured carbon materials.

- the formation of an ordered mesoporous network with pore diameters in the range 1–2 nm results from the incomplete filling of carbon in silica and from the decrease of carbon volume during the calcination step. The sucrose synthesis process leads to an incomplete filling of the porosity of the silica because of the presence of water and sulfuric acid and because of an autoactivation process during the calcination step (Vix-Guterl et al., 2003), this result in a higher total porous volume V_p compared to pitch method.
- the formation of a random microporous network is related to the carbon synthesis process itself. As expected, it can be seen in Table 2 that CVI method leads to the lowest value of the microporous volumes V_{N_2} and V_{CO_2}, while the sucrose impregnation allow the synthesis of materials with a high microporous volume.

The textural properties of the carbon materials can therefore be varied by changing the silica template and the carbon precursor as shown in Table 2.

We can see in Table 2 that for four of the five samples, the values of V_{N_2} are significantly higher than the microporous volume V_{CO_2}. This is typical of the presence of super micropores with diameters ranging between 1 and 2 nm (Dubinin, 1975).

2.2. *Hydrogen Adsorption*

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

Table 2. Textural characteristics of the carbon materials.

Sample	TSA (m^2/g)	V_P(cm^3/g)	V_{N_2} (cm^3/g)	$D_{p,BJH}$ (nm)	V_{CO_2} (cm^3/g)	$D_{p,DR}$ (nm)
CB15	754	0.50	0.23	3.34	0.26	0.85
CS15	1200	0.90	0.41	3.84	0.27	0.92
CPr15	711	0.76	0.20	4.78	0.09	1.04
CS48	2390	1.22	0.68	2.82	0.36	0.98
CB48	1130	0.64	0.33	4.02	0.18	0.93

adsorption capacity was computed from the amount of gas which desorbed from the material. The amount of hydrogen compressed in macropores was computed by assuming a density of 2 g/cm^3 for the carbon skeleton.

3. Results and Discussion

The measured adsorption capacities at 77 K are presented in Fig. 2. A comparison between our results obtained with nanostructured carbon materials and the hydrogen adsorption weight percentage on classical activated carbons (Zhou and Zhou, 2004; Texier-Mandoki et al., 2004) shows that all samples lead to similar results, i.e. around 4 wt% at 1 MPa. An exception to this observation are the carbon microbeads synthetized by Shao and coworkers (Shao et al., 2004) which allowed to store up to 7 wt% of hydrogen in similar experimental conditions. It must be noticed that the carbon material obtained by Shao et al. had a BET surface area of 3180 m^2/g and a pore volume equal to 1.9 cm^3/g, suggesting a highly microporous material.

From our results, it can be clearly seen that the carbon synthesis method has a great influence on the quantity of hydrogen adsorbed by the material. The lowest values are obtained with CVI method while sucrose impregnation synthesis leads to the highest. This observation can be done whatever the silica template used to build the replica. This results show the importance of the microporous structure of the material. As pointed out in the previous section, the formation of this microporosity is mainly related to the carbon precursor used for the material synthesis.

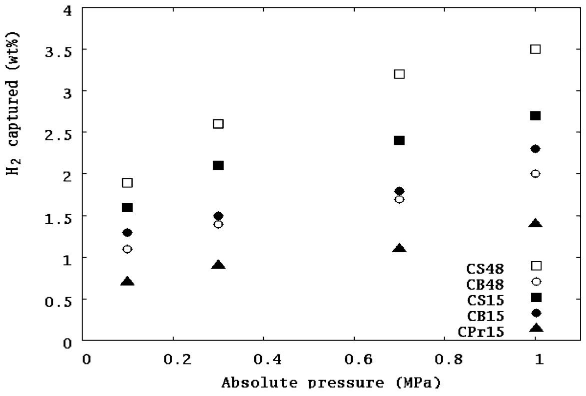

Figure 2. Hydrogen adsorption capacity of carbon materials at 77 K.

The influence of the silica template is less obvious. For an equivalent porous volume, the mesopore size and the wall thickness are greater for SBA-15 than for MCM-48. Then, it is expected that the mesopore size and the carbon wall thickness of the carbon replica of MCM-48 will be smaller. The consequence is that these samples have a higher BET surface area than the corresponding carbon materials built from SBA-15 silica (see Table 2). We can observe also that the porous volumes are higher for the material built from MCM-48 than the corresponding ones obtained by replication of SBA-15. The only exception is the sample CB-15 which have a high microporous volume V_{CO_2}. We can see that the hydrogen storage capacity is high for this material although the carbon material doesn't has a high porous volume V_P. Therefore, the ability to adsorb hydrogen at 77 K seems to be related to the range of micropores which is accessed by CO_2 adsorption.

The Fig. 3 presents the hydrogen adsorption capacity as a function of the microporous volume V_{CO_2}. It can be seen that there is a direct correlation between this characteristic of the material and its ability to adsorb hydrogen. De la Casa-Lilo and coworkers observed that there was a relation between the microporous volume V_{N_2} and the hydrogen storage capacity at room temperature (de la Casa-Lilo, 2003). Texier-Mandoki and co-workers showed however that V_{CO_2} is a better correlation parameter than V_{N_2} for activated carbons with high porous volumes (Texier-Mandoki et al., 2003).

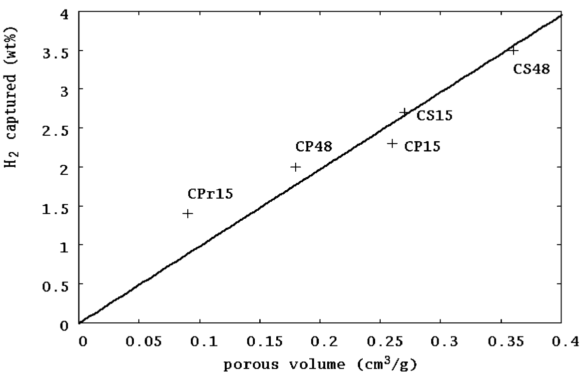

Figure 3. Influence of microporous volume on hydrogen adsorption capacity.

4. Conclusion

Nanostructured carbon materials have been prepared from two different silica templates and following three synthesis routes. This allowed to vary the textural properties of the materials. The hydrogen storage capacity of these materials was measured at 77 K between 0.1 and 1 MPa. In the case of ordered mesoporous carbon materials, it has been shown that there is a direct correlation between the microporous volume of the solid and its ability to adsorb hydrogen. Physical adsorption of hydrogen on such carbon materials is then clearly a process driven by the amount of nanometer sized pores. The characterization of this microporous volume through CO_2 adsorption at 273 K and Dubinin-Radushkevich analysis allow a good evaluation of the hydrogen storage capacity of these new carbon materials.

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