

Hydrogen Storage in Activated Carbons and Activated Carbon Fibers

M. A. de la Casa-Lillo, F. Lamari-Darkrim,[†] D. Cazorla-Amorós, and A. Linares-Solano*

Departamento de Química Inorgánica, Universidad de Alicante, Apdo. 99, Alicante, Spain

Received: December 18, 2001; In Final Form: July 27, 2002

Hydrogen storage has been studied in a large variety of activated carbons and activated carbon fibers and a wide range of pressures (up to 70 MPa). The experimental technique used has good reliability, and the experiments performed have a small error and high reproducibility. This seems to be essential to get trustworthy conclusions. In these samples, we have not found large amounts of hydrogen adsorbed. In any case, an activated carbon derived through a simple preparation method provides hydrogen storage values at 10 MPa close to 1 wt % (i.e., a value close to the target from an application point of view). The experimental results have been compared with theoretical work found in the literature, and an important agreement can be observed. From this study, we conclude that the optimum pore size for hydrogen storage is that which can hold two layers of adsorbed hydrogen. This work also considers practical aspects related to hydrogen storage in activated carbons and activated carbon fibers.

1. Introduction

Hydrogen is an ideal alternative to fossil fuels from an environmental point of view^{1–4} because its combustion does not generate pollutants such as particles, nitrogen oxides, sulfur oxides, hydrocarbons, and carbon monoxide.² From an economic point of view, the use of hydrogen could revolutionize energy and transportation markets, which is what generates great interest toward this fuel. This interest has led to the so-called “hydrogen economy”.

However, the main drawback for the use of hydrogen as a transportation fuel or in power generation is the storage of this gas to reach a sufficiently high energy density that could fit to the goals of the DOE hydrogen plan for automotive fuel cell systems (i.e., 6.5 wt % of H₂).⁵ There are essentially four ways to store hydrogen: liquefaction, compressed gas, metal hydrides, and adsorption.

Hydrogen liquefaction, using a temperature of 21 K, permits us to reach high densities, but it is very expensive and consumes great amounts of energy.⁶ The second possibility, compressed gas,⁷ is cheaper than liquid hydrogen but requires higher volumes and heavier containers to get a similar hydrogen density. In fact, it needs 4 or 5 times the volume of the present gasoline tank (i.e., about 250 L) and a safe and heavy container that can support 40 MPa of pressure.⁸ The large volume of the tank and the risks of the use of high pressures of hydrogen in conventional vehicles mean that compressed gas cannot be the definitive solution.⁹

The third form to store hydrogen is by metallic hydrides.^{6,10–14} It has the advantage of the low pressures used, but the storage system (i.e., tank plus metallic compound) is heavy and, additionally, they must be heated to recover the hydrogen stored. These two reasons indicate that metallic hydrides are not the best solution for this purpose.

The last possibility, hydrogen adsorption in porous solids and specially activated carbons, is still considered one interesting alternative.^{5,15–19} Initially, the studies carried out were based

on the use of cryogenic systems, which are not useful from an economic point of view.¹⁵ Recently, research has focused on the search for the ideal adsorbent that, used at room temperature, allows the storage of interesting amounts of H₂.⁵

Among the materials that can be used as adsorbents, carbon materials such as activated carbons, carbon nanotubes, and carbon nanofibers have been the subject of research. The results obtained are, in many cases, different and striking.^{20–23} In fact, values as large as 60 wt % for graphite nanofibers²⁴ or between 5 and 10 wt % for nanotubes²⁵ have been reported. These values have been neither reproduced nor explained by theoretical calculations.^{19,26} This suggests that the reliability of the experimental technique to obtain the amount of hydrogen adsorbed or retained by the carbon material is essential.

In previous studies,^{19,26} the hydrogen storage capacity of microporous carbon materials was analyzed theoretically and experimentally for a selection of samples. The results allowed us to conclude that there exist an optimum pore size and an optimum pore geometry (slit pore) for hydrogen adsorption, and theoretical values for hydrogen adsorption as large as those reported in the literature were never obtained. However, some discrepancies exist between the theoretical results obtained regarding the optimum size of the pores for hydrogen adsorption. In ref 26, the optimum pore size can hold one layer of adsorbed H₂ (the proposed pore size is close to 0.35 nm), whereas in ref 19, the optimum pore size can hold two layers of adsorbed hydrogen (the proposed pore size is close to 0.56 nm).

Then, the objective of the present work is to evaluate the hydrogen storage capacity for a wide variety of activated carbon fibers and microporous activated carbons with different pore-size distributions and packing densities and up to higher pressures than previously reported (i.e., 6 MPa in ref 26). To elucidate the optimum size of pores for hydrogen storage, we will compare our results with those obtained with compressed hydrogen and with the theoretical calculations previously performed.^{19,26}

2. Experimental Section

Several activated carbon fibers (physically activated with CO₂ and steam), chemically activated carbon, several coal-based

* Corresponding author. E-mail: linares@ua.es.

[†] LIMHP-CNRS (UPR 1311), Université Paris 13, Avenue J. B. Clement 93430 Villetaneuse, France.

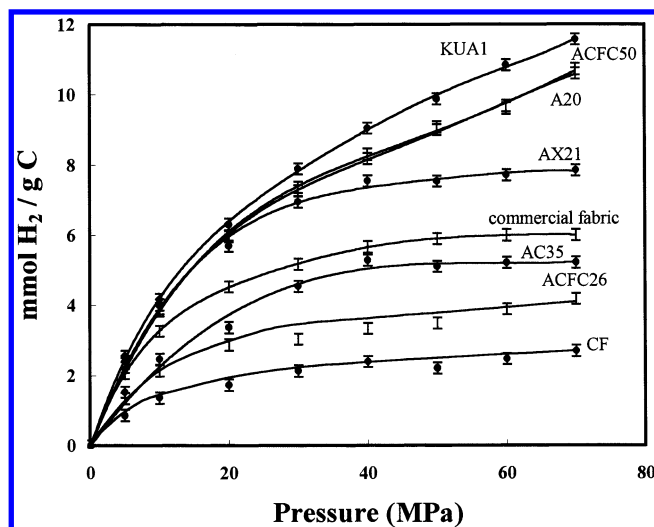


Figure 1. Hydrogen adsorption isotherms at 293 K and up to 70 MPa.

samples, and commercial coal tar pitch-based activated carbon fibers have been used in this study as adsorbents for hydrogen storage. All of them are essentially microporous materials with a negligible contribution of meso- and macroporosity.^{27,28}

Porous texture analysis of the different materials was carried out by N₂ and CO₂ adsorption at 77 and 273 K in an Autosorb 6 apparatus. Micropore volumes have been calculated from the application of the Dubinin–Radushkevich (DR) equation to both adsorption measurements.²⁹ The mean pore size was deduced from the characteristic energy.^{30–33}

The hydrogen adsorption measurements were performed using a mixed gravimetric and volumetric method and up to 70 MPa. Blank runs performed with the empty cell correspond to the calculated amount of hydrogen compressed in the volume of the sample cell. These blank runs show that the sample cell does not adsorb hydrogen and that the system works properly. By considering that the correct measurement of hydrogen adsorption at high pressures is essential to achieving a proper evaluation of a given material, we have included a detailed description of the experimental procedure and the equipment used in this work. The samples were degassed prior to the high-pressure measurements in vacuum (10^{−10} MPa) at 673 K for 48 h. For the hydrogen adsorption experiments, a sample cell of a well-known volume is connected to a high-pressure system and is hanging in a balance connected to a computer (the sensitivity of the balance is 1 mg). The temperature of the cell is maintained at 293 K during the adsorption. Hydrogen is introduced up to the desired pressure, and when thermodynamic equilibrium is reached, the value of the weight indicated by the balance is collected. The measured weight increase corresponds to the hydrogen adsorption in the pores and to compressed hydrogen. From this value, the amount of hydrogen adsorbed is calculated using the weight of sample, the helium density of the carbon material, and the volume of the sample cell. The

isotherms obtained for the carbon samples are plotted in Figure 1. The isotherms include the error bars for each data point to show the reliability of the experiments. The experiments with this equipment have been compared with a gravimetric system that works up to 5 MPa, giving very similar values (the error within is 5%). This second piece of equipment has been calibrated for hydrogen adsorption measurements by using Pd as a calibration standard. Pd powder (5 g) was contacted with H₂ (0.1 MPa) at 293 K, giving a H/Pd value of 0.72 ± 0.03, which is very close to that reported in the literature (i.e., H/Pd = 0.73³⁴).

The packing density of these materials was determined by pressing a given amount of sample (in the range 0.5–0.2 g) in a mould with a cross-sectional area of 1.31 cm² and a load of 1000 kg and using a cylindrical rod for pressing. The measurement of the height of the rod with the mould empty and with sample permits the evaluation of the volume of the material and, then, the packing density. The difference of heights obtained vary from 0.38 to 0.19 cm. The measurements were repeated several times. The densities obtained have an error smaller than 3%.

3. Results and Discussion

3.1. Adsorption of Hydrogen Versus Porous Texture of the Carbonaceous Materials. Table 1 summarizes the porous texture of the materials used, including the BET surface area, the volume of micropores from the adsorption of N₂ at 77 K and CO₂ at 273 K, the mean pore size,^{32,33} the packing density (which measures the weight of sample per volume of tank), and the helium density of the samples determined at 673 K and atmospheric pressure in a volumetric system³⁵ (which measures the weight of sample per volume of both carbon atoms and blocked pores).

The porous texture of the different materials (Table 1) shows that all the samples used have a high micropore volume except for the nonactivated carbon fiber (sample CF). Additionally, the carbon materials selected cover a wide range of micropore sizes, from the nonactivated CF with a very narrow porosity that is not accessible to nitrogen at 77 K to samples with a mean pore size of 1.5 nm. Table 1 also includes the density of adsorbed hydrogen inside the pores and the total volumetric storage capacity at 10 MPa (Ms) obtained from hydrogen adsorption experiments such as those compiled in Figure 1. The density of adsorbed hydrogen corresponds to the amount of adsorbed hydrogen per volume of micropores (this is the space in which hydrogen can be adsorbed); Ms is the total amount of hydrogen that can be stored per volume of the tank, including the compressed hydrogen. The hydrogen adsorption isotherms of the samples at 293 K and up to 70 MPa have similar shapes and are of type I according to the IUPAC classification.³⁶ Figure 2 includes the amount of hydrogen adsorbed (weight percent) versus the volume of micropores (cc/g) for the studied samples. This Figure shows the results obtained at 10 and 70 MPa of

TABLE 1: Porous Texture of the Carbon Materials Studied

sample	BET area (m ² /g)	DR volume N ₂ (cc/g)	DR volume CO ₂ (cc/g)	mean pore size (nm)	packing density (g/cm ³)	helium density (g/cm ³)	hydrogen adsorbed density (10 MPa) (kg/m ³)	Ms 10 MPa (kg/m ³)
CF	0	0	0.18	0.41	1.22	1.70	15.34	6.3
ACFC26	1079	0.39	0.39	0.75	1.04	1.70	10.89	8.2
ACFC50	1738	0.78	0.57	1.36	0.72	1.85	10.12	10.5
KUA1	1058	0.51	0.50	0.66	1.01	1.73	16.34	11.8
A20	2206	0.79	0.43	1.46	0.76	1.95	9.86	10.7
fabric	1407	0.65	0.54	1.46		1.70	10.15	
AC35	1204	0.54	0.40	1.54		1.83	9.26	
AX21	2575	0.86	0.68	1.48		1.70	9.41	

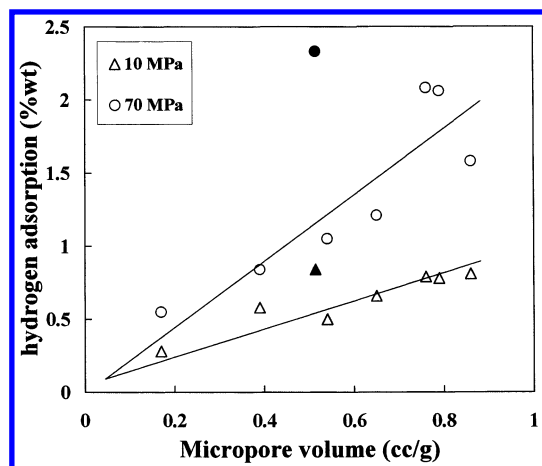


Figure 2. Amount of adsorbed hydrogen (wt %) versus micropore volume at 10 and 70 MPa (filled points correspond to sample KUA1).

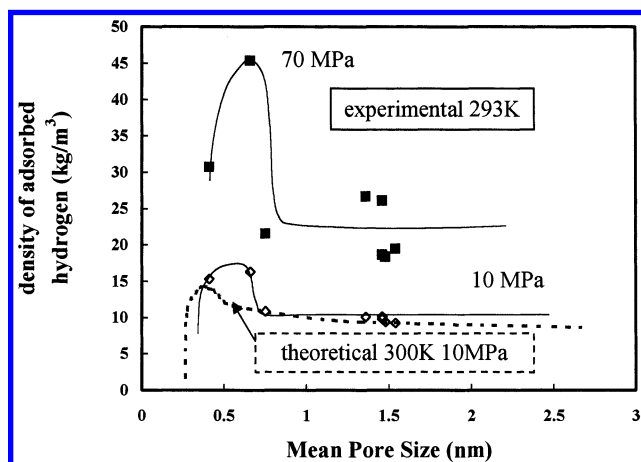


Figure 3. Density of adsorbed hydrogen inside the pores (kg/m^3) versus mean pore size (— — —, theoretical results).

hydrogen pressure. Essentially, the hydrogen adsorption increases with the volume of micropores, except in the case of sample KUA1. We must emphasize the greater hydrogen adsorption capacity of sample KUA1, which was obtained from the chemical activation with KOH of a Spanish anthracite through a simple activation method,³⁷ compared to that of other commercial materials such as activated carbon AX21 (also derived from chemical activation with KOH), which is considered to be one of the activated carbons available on the market with the highest adsorption capacity.

The results for sample KUA1, which adsorbs higher amounts of hydrogen than expected from its micropore volume, indicate that the pore size may have a large influence on the amount adsorbed, as already indicated by theoretical calculations.^{19,26} In this sense, Figure 3 plots the hydrogen density inside the micropores measured experimentally (293 K and pressures of 10 and 70 MPa) versus the mean pore size of the samples. The Figure also includes, for comparison purposes, the theoretical results (at 300 K and 10 MPa).²⁶ In the experimental results, the mean pore size has been determined from gas adsorption (N_2 and CO_2 at 77 and 273 K, respectively) at subatmospheric pressures. It must be emphasized that the experimental curve matches quite well to the theoretical calculations. In both cases, a maximum in the density of adsorbed hydrogen is found as a function of the pore size. The optimum theoretical pore size to store hydrogen is 0.36 nm according to ref 26 (i.e., a pore that can hold one layer of adsorbed H_2) and 0.56 nm according to ref 19 (i.e., a pore that can hold two layers of hydrogen). The

experimental values of Figure 3 provide 0.66 nm, which is much closer to the calculations carried out by Wang and Johnson.¹⁹

In this sense, it must be noted that the method used in this work to estimate the mean pore size from the adsorption isotherms produces results that are in quite good agreement with experimental evidence. In fact, the pore size calculated for the sample CF (i.e., nonactivated carbon fiber) is 0.41 nm (Table 1), and this is a material that exhibits molecular sieve properties for CO_2 and CH_4 separation.³⁸ This means that the pore size should be between 0.33 and 0.38 nm (i.e., kinetic diameters for CO_2 and CH_4 , respectively).³⁸

The experiments demonstrate that the density of adsorbed hydrogen is strongly dependent on the pore size and that there exists an optimum pore size where hydrogen adsorption is greater because of the enhanced adsorbate–adsorbent interactions. The optimum pore size seems to be that able to accommodate two layers of adsorbed H_2 . The results also point out that the amount of hydrogen adsorbed at room temperature and moderate pressures (10 MPa) depends on the volume of micropores of the adsorbent. Moreover, these experiments show that the hydrogen adsorption depends on the micropore volume and pore size, but it is not affected by the preparation method of the activated carbon (i.e., physical or chemical activation) or the material shape (i.e., powder or fiber).

Moreover, the analysis of hydrogen adsorption data in these samples (among which a material with a pore size close to the optimum and a high micropore volume has been included) shows that the values are much lower than those published previously by Dillon et al.²⁵ and by Chambers et al.²⁴ using nanotubes and nanofibers, respectively. The high amounts of hydrogen stored in the experiments reported in ref 24 (i.e., 200 times higher than that calculated theoretically and the results obtained with our samples) indicate that either the mechanism of adsorption is different from physical gas adsorption or that more experimental work is necessary, according to the contradictory experimental and theoretical results obtained by other authors.^{19,39}

3.2. Hydrogen Storage in Activated Carbons and Activated Carbon Fibers. In the previous section, we have dealt with hydrogen adsorption from a fundamental point of view by taking into account aspects related to the pore size and pore volume of the adsorbents. In this section, we will discuss practical issues related to hydrogen storage in activated carbons and activated carbon fibers.

From this point of view, it is most interesting to maximize the amount of hydrogen adsorbed by unit of tank volume and to define the range of pressures in which the contribution of hydrogen adsorption is larger than that of compression. Thus, we will use the total volumetric storage capacity (Ms), calculated as the amount of hydrogen stored by volume of tank (this parameter includes both the hydrogen adsorbed and the hydrogen compressed).

Figure 4 includes the total volumetric storage capacity, Ms, for each adsorbent used and the contribution of pure gas compression (dotted line) versus the pressure. This plot clearly shows that the samples ACFC50, A20, and KUA1 store larger amounts of hydrogen than does compressed hydrogen at the same pressure and temperature. The Figure also contains (i.e., second y axis) the ratio between the total volumetric storage capacity and the density of hydrogen gas versus the pressure. It can be observed that at low pressure the adsorption is more effective (this ratio is higher than 1) than pure compression for all the samples except for CF and that it depends on the type of adsorbent. Thus, for the samples with higher micropore volumes,

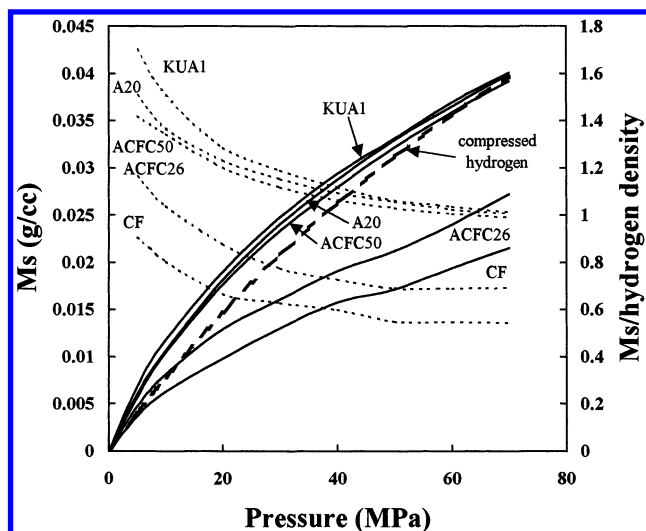


Figure 4. Total volumetric storage capacity M_s (g/cm^3) (—, left y axis) and $M_s/\text{density}$ of compressed hydrogen (---, right Y axis) versus pressure (MPa).

the calculated ratio follows this order: $\text{KUA1} > \text{A20} \approx \text{ACFC50}$, which is a consequence of the differences in pore size (Table 1).

The values of M_s for a pressure of 10 MPa, gathered in Table 1, allow us to observe that the maximum total volumetric storage capacity as well as the maximum density of adsorbed hydrogen correspond to sample KUA1, in which the pore size is close to the optimum for hydrogen storage. In sample CF (that is, the nonactivated carbon fibers), in which the pore size is close to the size that could hold one layer of adsorbed H_2 , the density of adsorbed hydrogen is high, but the volume of micropores is small enough to obtain an acceptable total volumetric hydrogen storage capacity (i.e., M_s). Then, for application purposes, not only the pore size but also the pore volume per volume of tank is important in achieving high hydrogen storage.

To get an idea of the improvement that supposes the adsorption with respect to the compression for the best sample studied (sample KUA1), it is illustrative to indicate the pressure that each system (adsorption and compression) should use to store the same amount of hydrogen. Thus, $6.9 \text{ kg}/\text{m}^3$ of hydrogen can be stored at 5 MPa by adsorption and at 9 MPa by compression. To store $11.8 \text{ kg}/\text{m}^3$ of hydrogen, 10 MPa is necessary by adsorption, and 15 MPa, by compression. For $15.3 \text{ kg}/\text{m}^3$ of hydrogen, 15 MPa is required by adsorption, and 22 MPa, by compression; finally, to store $19 \text{ kg}/\text{m}^3$ of hydrogen, 20 MPa is needed by adsorption, and 27 MPa, by compression. The smaller pressure required in the adsorption system results in safer hydrogen storage and a decrease in the weight of the tank because thinner walls could be used.

To have vehicles with sufficient driving range, which would be competitive with the present fossil fuel market (300–600 km), about 5 kg of hydrogen should be used in an internal combustion engine.⁴⁰ At room temperature, it would occupy 227 L at 34.5 MPa and 340 L at 20 MPa.⁴⁰ With the adsorption system and the results obtained for sample KUA1, the tank volume can be decreased to 185 L at 34.5 MPa and 263 L at 20 MPa.

Thus, the amount of hydrogen necessary to have a driving range between 300 and 600 km could be stored in a tank of 250 L by using an appropriate carbonaceous adsorbent and a pressure of 20 MPa. This pressure is currently being used in conventional hydrogen bottles. If we consider that most travel is shorter than 100 km, then the same volume could be used

with a pressure of 5 MPa, which is much more convenient for safety reasons.

4. Conclusions

Detailed experimental work on hydrogen adsorption in a large variety of activated carbons and activated carbons fibers and a wide range of pressure has been carried out. The experimental results match fairly well with theoretical studies found in the literature (i.e., refs 19 and 26) and confirm that the optimum pore size for hydrogen adsorption in porous carbons is that which can hold two layers of adsorbed hydrogen (i.e., pore size of about 0.6 nm).

Extremely large amounts of hydrogen adsorption, such as those reported in refs 24 and 25, have not been measured in any of the samples analyzed. The highest values of hydrogen adsorption in activated carbons or activated carbon fibers are close to 1 wt % at 10 MPa. This value corresponds to an activated carbon obtained from an anthracite and through a simple preparation method.

The comparison between hydrogen storage in porous carbons and compressed hydrogen indicates that the range of pressure that is useful for the application of the adsorption system is between 5 and 20 MPa.

Acknowledgment. We thank DGICYT and MCYT for financial support (projects AMB1999-1595-CE and MAT2000-0621).

References and Notes

- (1) Appleby, A. J. *Int. J. Hydrogen Energy* **1997**, *19*, 175.
- (2) Contreras, A.; Yigit, S.; Özyay, K.; Veziroglu, T. N. *Int. J. Hydrogen Energy* **1997**, *22*, 1053.
- (3) Nicoletti, G. *Int. J. Hydrogen Energy* **1995**, *20*, 759.
- (4) Appleby, A. J. *Sci. Am.* **1999**, *281*, 58.
- (5) Hynek, S.; Fuller, W.; Bentley, J. *Int. J. Hydrogen Energy* **1997**, *22*, 601.
- (6) Das, L. M. *Int. J. Hydrogen Energy* **1996**, *21*, 789.
- (7) CALORIC, INFORM 1993; Vol. 4, No. 12.
- (8) Rodriguez, N. M.; Baker, R.; Terry, K. U.S. Patent 5,653,951, 1997.
- (9) Swain, M. R.; Shriver, J.; Swain, M. N. *Energy Fuels* **1998**, *12*, 83.
- (10) Fukai, Y. In *The Metal-Hydrogen System*; Gonser, U., Ed.; Springer Series in Material Science; Springer-Verlag, New York, 1993.
- (11) Imamura, H.; Sakasai, N. *J. Alloys Compd.* **1995**, *231*, 810.
- (12) Gross, K. J.; Spatz, P.; Züttel, A.; Schlappbach, L. *J. Swiss Soc. Surf. Mater.* **1996**, *5*, 22.
- (13) Imamura, H.; Sakasai, N.; Kajii, Y. *J. Alloys Compd.* **1996**, *232*, 218.
- (14) Imamura, H.; Sakasai, N.; Fujinaga, T. *J. Alloys Compd.* **1997**, *253–254*, 34.
- (15) Carpetis, C.; Peschka, W. *Int. J. Hydrogen Energy* **1980**, *5*, 539.
- (16) Noh, J. S.; Agarwal, R. K.; Schwarz, J. A. *Int. J. Hydrogen Energy* **1987**, *12*, 693.
- (17) Chahine, R.; Bose, T. K. *Int. J. Hydrogen Energy* **1994**, *19*, 161.
- (18) Zhou, Y.; Zhou, L. *Sci. China, Ser. B* **1996**, *39*, 598.
- (19) Wang, Q.; Johnson, J. K. *J. Chem. Phys.* **1999**, *110*, 577.
- (20) Jarvi, T. D.; Sun, J.; Conosposk, L. F.; Satyapal, S. *Prepr. Symp. Am. Chem. Soc., Div. Fuel Chem.* **1999**, *44*, 962.
- (21) Ye, Y.; Ahn, C. C.; Witham, C.; Fultz, B.; Liu, J.; Rinzler, A. G.; Colbert, D.; Smith, K. A.; Smalley, R. E. *Appl. Phys. Lett.* **1999**, *74*, 2307.
- (22) Lamari, M.; Malbrunot, P. *AIChE J.* **2000**, *46*, 632.
- (23) Darkrim, F.; Levesque, D. *J. Phys. Chem. B* **2000**, *104*, 6773.
- (24) Chambers, A.; Park, C.; Baker, T. K.; Rodriguez, N. M. *J. Phys. Chem. B* **1998**, *102*, 4253.
- (25) Dillon, A. C.; Jones, K. M.; Bekkedahl, T. A.; Klang, C. H.; Bethune, D. S.; Heben, M. J. *Nature (London)* **1997**, *386*, 377.
- (26) Rzepka, M.; Lamp, P.; de la Casa-Lillo, M. A. *J. Phys. Chem. B* **1998**, *102*, 10894.
- (27) Alcañiz-Monge, J.; Cazorla-Amorós, D.; Linares-Solano, A.; Yoshida, S.; Oya, A. *Carbon* **1994**, *32*, 1277.
- (28) Alcañiz-Monge, J.; Cazorla-Amorós, D.; Linares-Solano, A. *Carbon* **1997**, *35*, 1665.
- (29) Dubinin, M. M. *Chemistry and Physics of Carbon*; Walker, P. L., Jr., Ed.; Marcel Dekker: New York, 1966; Vol. 2, p 51.

- (30) Dubinin, M. M. *Chem. Rev.* **1960**, 60, 235.
- (31) Stoeckli, F.; Ballerini, L. *Fuel* **1991**, 70, 557.
- (32) Dubinin, M. M. *Carbon* **1985**, 23, 373.
- (33) Cazorla-Amorós, D.; Alcañiz-Monge, J.; de la Casa-Lillo, M. A.; Linares-Solano, A. *Langmuir* **1998**, 14, 4589.
- (34) Frieske, H.; Wicke, E. *Ber. Bunsen-Ges. Phys. Chem.* **1973**, 77, 48.
- (35) Malbrunot, P.; Vidal, D.; Vermesse, J.; Chahine, R.; Bose, T. K. *Langmuir* **1997**, 13, 539.
- (36) Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemieniowska, T. *Pure Appl. Chem.* **1985**, 57, 603.
- (37) Lozano-Castelló, D.; Lillo-Rodenas, M. A.; Cazorla-Amorós, D.; Linares-Solano, A. *Carbon* **2001**, 39, 741.
- (38) de la Casa-Lillo, M. A.; Alcañiz-Monge, J.; Raymundo-Piñero, E.; Cazorla-Amorós, D.; Linares-Solano, A. *Carbon* **1998**, 36, 1353.
- (39) Ahn, C. C.; Ye, Y.; Ratnakumar, B. V.; Witham, C.; Bowman, R. C., Jr.; Fultz, B. *Appl. Phys. Lett.* **1998**, 73, 3378.
- (40) Berry, G. D.; Aceves, S. M. *Energy Fuels* **1998**, 12, 49.