

MICROPOROUS CARBONS FOR GAS-STORAGE APPLICATIONS

*Marek A. Wójtowicz, Wayne W. Smith, Michael A. Serio,
Girard A. Simons* and Ware D. Fuller†*
Advanced Fuel Research, Inc., 87 Church Street, East Hartford, CT 06108
**Simons Research Associates, 3 Juniper Road, Lynnfield, MA 01940*
†Arthur D. Little, Inc., 20 Acorn Park, Cambridge, MA 02140-2390

Introduction

Gas storage by adsorption on activated carbon is possible at relatively low pressures using carbons with a well developed microporosity. The tremendous potential of gas adsorption was recognized, but never realized in practice [1], presumably due to the difficulties with restricting the growth of meso and macroporosity during char activation. The traditional char-activation methods include: (1) steady-state steam or carbon dioxide gasification; and (2) chemical treatment of carbon precursors. In both cases, wide distributions of pore sizes are usually obtained, mainly due to pore widening that occurs at the pore entrance. In principle, mass-transfer limitations could be eliminated by running the activation process in a kinetically-controlled régime. This is unrealistic, however, due to the long time scales that would be required by such a process. In this paper, a novel char-activation technique is described which eliminates problems with pore-mouth widening and allows for a uniform pore development until the desirable pore size is reached. In combination with traditional methods, the technique could be used to tailor the pore-size distribution to meet specific user-defined requirements.

Char Activation via Alternating Transient Adsorption and Desorption

The transient technique involves alternating cycles of low-temperature chemisorption (e.g., oxygen from air at ~ 150 °C) and high-temperature desorption in an inert atmosphere. In this way, advantage can be taken of the rapid chemisorption kinetics on a fresh surface, followed by fast desorption of surface oxides at high temperatures. Both the low temperature of the chemisorption step and the inert atmosphere of the desorption step prevent excessive burn-off and the creation of larger pores. In each chemisorption step, this method allows deep penetration of the activating agent (CO_2 , H_2O , or O_2) into the smallest pores, without the preferential burn-off of carbon at the pore mouth. It is also possible that through the uniform coverage of the char surface, the proposed technique leads to the preferential initiation of new micropores rather than the enlargement of the existing ones.

The transient technique allows for the activation of larger char particles without the onset of pore-mouth widening. In the steady-state activation, the latter phenomenon is known to be a problem of increasing severity as the particle size increases. Large sorbent particles are advantageous in gas-storage applications due to the potentially improved sorbent packing efficiency and the lower pressure drop during gas discharge and refilling. The packing efficiency could be improved by up to 40% if cubical sorbent elements were stacked inside the container instead of randomly packed spherical (or nearly spherical) particles. The modeling of hydrogen transport through a bed of stacked 5 mm cubes of microporous sorbent has shown that the proposed concept is feasible for container dimensions of the order of one meter [2].

Several microporous sorbents have been prepared using the transient adsorption-desorption technique and characterized in terms of adsorption isotherms and hydrogen-storage capacity and delivery rates. The results are summarized below.

Experimental

Phenol-formaldehyde and polyvinylidene chloride (PVDC) were used as carbon precursors, and the carbonization conditions were: 1 atm helium, 1373 K, and 15-30 min hold time in a tube furnace. The activation step was carried out in a thermogravimetric analyzer (TGA) or in a packed-bed reactor, both interfaced with a personal computer to control temperature and gas environment (a flow of air in the low-temperature chemisorption step, and helium in the high-temperature desorption step). The chemisorption and desorption temperatures were 423-473 K and ~ 1273 K, respectively. The number of the required chemisorption-desorption cycles was a function of the desired degree of burn-off, sample reactivity, and process conditions. The current burn-off could be followed using the TGA weight-loss data. Adsorption isotherms were collected using an automated DigiSorb 2600 analyzer (Micromeritics). One sorbent was tested for hydrogen-storage performance at the state-of-the-art facility at Arthur D. Little, Inc. The experimental set-up and procedures are described in

reference [1b]. It should be noted that only the amount of adsorbed hydrogen that can be desorbed (delivered) on realistic time scales is reported.

Results and Discussion

A nitrogen adsorption isotherm of one of the PVDC carbons obtained in this study is shown in Fig. 1. An adsorption isotherm of a Japanese superactivated carbon is also shown for comparison. It is evident that both carbons have Type I isotherms characteristic of highly microporous materials. Although the degree of burn-off for the PVDC char is as high as 68%, no appreciable mesoporosity can be observed, which is exactly what was intended. The pore volumes and BET surface areas were found to be quite similar for both carbons. It should be noted, however, that the PVDC char activated using the transient adsorption-desorption technique has a particle size one order of magnitude larger than the reference carbon. It is doubtful whether large particles with such a high degree of microporosity could be obtained using the traditional steady-state activation. Although our transient technique has not yet been applied to particles larger than 0.4 mm, model predictions indicate that particle sizes as large as 5 mm are readily attainable [2].

Results of the hydrogen-storage tests are presented in Fig. 2. They are expressed in terms of the usable capacity ratio (a ratio of the amount of hydrogen available from a carbon-filled tank to the amount of hydrogen available from an "empty" tank of the same volume). P1 is the gas-storage pressure, and P2 is the pressure at the receiving end of the hydrogen-delivery train. Performance curves for one of our carbons (AFR carbon) can be compared with those of the best-performing sorbent studied to date (carbon E) [1b]. Data in Fig. 2 show that, on a volumetric basis, our carbon has similar hydrogen-storage characteristics as carbon E, but, due to the difference in carbon densities (0.25 versus 0.74 g/cm³), our material is three times better on a gravimetric basis. Carbon E was previously shown to outperform other sorbents by a wide margin [1b].

Conclusions

The available preliminary data demonstrate a good potential of the novel char-activation technique. Highly microporous carbons with nitrogen BET surface areas up to 2000 m²/g and particle sizes up to 0.425 mm were obtained. Excellent hydrogen-storage performance was demonstrated. On a volumetric basis, our carbon performed as well as the best carbon studied to date [1b]. On a gravimetric basis, our carbon was better by a factor of three.

Acknowledgment

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References

1. *Multi-Fuel Reformers for Fuel Cells Used in Transportation: Assessment of Hydrogen Storage Technologies*, Arthur D. Little, Inc., Cambridge, MA, (a) Ph. I report (DOE/CE50343-1), 1994; (b) Ph. II report (DOE/CE50343-3), 1995.
2. Wójtowicz, M.A., Smith, W.W., Serio, M.A. and Simons, G.A., Gas Storage Using Microporous Carbon Adsorbents. Ph. I final report, NASA contract No. NAS9-19470, 1996.

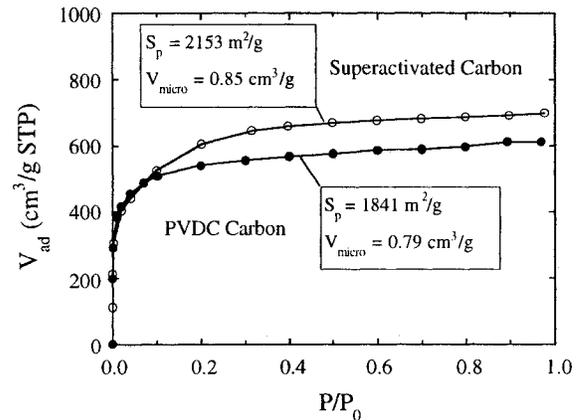


Figure 1. Nitrogen adsorption isotherms of (a) a PVDC carbon (68% burn-off; $d_p = 0.300\text{--}0.425$ mm); and (b) a Japanese superactivated carbon ($d_p \approx 0.018$ mm). S_p and V_{micro} are N₂ BET specific surface area and micropore volume, respectively.

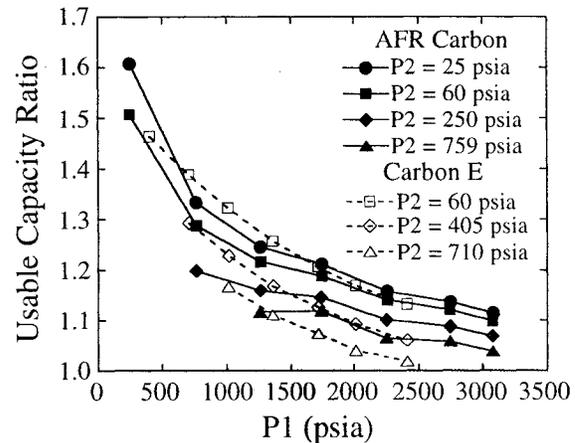


Figure 2. The usable capacity ratio for the AFR carbon and for carbon E at 300 K.