MECHANISM OF ENHANCED HYDROGEN ADSORPTION ON PALLADIUM-DOPED NANOPOROUS CARBON FIBERS

Cristian I. Contescu[1], Nidia C. Gallego[1], Xianxian Wu[1], Halil Tekinalp[2], Dan D. Edie[2],
and Frederick S. Baker[1]
[1]Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA; [2]Clemson University, Clemson, SC 29630, USA

Abstract

Recent work at Oak Ridge National Laboratory was directed towards adsorptive storage of hydrogen in nanoporous carbon fibers in which palladium was incorporated prior to spinning and carbonization/activation of the fibers. Palladium-doped carbon fibers exhibited emhanced hydrogen uptake compared to the corresponding palladium-free nanoporous carbon fibers (at room temperature and 2 MPa pressure). However, the mechanism responsible for the enhanced hydrogen uptake is not fully understood. New findings are presented in this paper in support of a mechanism that encompasses both hydrogen spillover on palladium metal sites and hydrogen physisorption on nanostructured carbon sites.

Introduction

Efficient storage of hydrogen for use in fuel cell-powered vehicles is a challenge that is being addressed in different ways, including adsorptive, compressive, and liquid storage approaches. However, none of these hydrogen storage methods have met all of the U.S. Department of Energy (DOE) targets with respect to weight and volumetric storage capacity, temperatures of efficient cyclic operation, cost, and safety requirements that would allow large scale implementation for either transportation of utility use. Hydrogen storage by adsorption in nanostructured carbon continues to attract a renewed interest because of the significant advantage offered by this light weight and reasonably inexpensive material.

After a few optimistic reports emerged in early 90's, indicating that large hydrogen storage capacities could be achieved on nanostructured carbons, approaching or exceeding the 6.0 wt% target set by DOE for the storage system, these first results could not be reproduced by other researchers. At Oak Ridge National Laboratory (ORNL), a variety of carbon materials have been evaluated for hydrogen storage, including commercial activated carbons, activated carbon fibers (ACF), activated carbon fiber composites, and single wall carbon nanotubes (Gallego, 2004[1]). None of these carbon materials have shown significant H_2 uptake. At ambient temperature and moderate pressure (2MPa) the uptake values were typically < 0.2 wt%, with the exception of a wood-based activated carbon exhibiting the highest value of ~ 0.3 wt%. More promising results were obtained with carbon materials modified by doping with a small amount of a transition metal. Metal-assisted cold storage of hydrogen is known from late 80's (Schwarz, 1988[2]) but is not practical because of the cryogenic temperatures involved. Preliminary work on this approach at ORNL produced encouraging results. It was found that, at ambient temperature and a maximum pressure of 2 MPa, Pd-doped activated carbon fibers (Pd-ACF) exhibit enhanced hydrogen storage capacity which corresponds to H/Pd ratios much in excess of what is expected for unsupported, bulk Pd metal (Gallego, 2005[3]). Further work, directed to understanding the mechanisms of enhanced hydrogen uptake on Pd-doped activated carbon fibers in comparison to the Pd-free counterparts, confirmed the effect of metal doping, although was not successful in reproducing the high uptake levels reported initially. The effort directed on understanding and controlling the state of Pd in Pd-ACF materials demonstrated that Pd is present as dispersed nanoparticles (3-5 nm) which reversibly convert into Pd hydride on exposure to hydrogen at room temperature. However, partial sintering of Pd into larger particles was found as the temperature of heat treatment steps (carbonization, activation) exceeded a threshold of about 850 ºC (Gallego, 2006).[4] Based on the known properties of Pd as a catalyst for hydrogen dissociation, it was postulated that the enhancement of hydrogen uptake by Pd-doped ACF is the effect of a spillover effect, a mechanism already recognized in previous reports on metal-assisted hydrogen adsorption (Robell, 1964[5]; Boudart, 1970[6]) and storage on various carbon materials (Lueking, 2004[7]; Zacharia, 2005[8]; Anson,

---

[1] Gallego, N. C., Burchell, T. D., Clark, A. M. (2004). Carbon materials for hydrogen storage, in Extended Abstracts, Carbon 2004 (Providence, RI, USA): American Carbon Society.

[2] Schwarz, J. A. (1998). Metal assisted carbon cold storage of hydrogen, US Patent 4,716,736 (Jan. 5, 1988).

[3] Gallego, N. C., Contescu, C. I., Baker, F. S., Basova, Y. V., Edie, D. D. (2005). Mechanisms of metal-assisted hydrogen storage in nanostructured carbons, in Extended Abstracts, Carbon 2005 (Gyeoungju, Korea): Korean Carbon Society.

[4] Gallego, N. C., Baker, F. S., Contescu, C. I., Wu, X., Speakman, S. A., Tekinalp, H., Edie, D. D., Effect of Pd on the hydrogen adsorption capacity of activated carbon fibers, in Extended Abstracts, Carbon 2006 (Aberdeen, Scotland): British Carbon Group

[5] Robell, A. J., Ballou, E.V. and Boudart, M. (1964) Surface diffusion of hydrogen on carbon, *J. Phys. Chem.*, 68, 2748-2753.

[6] Boudart, M., Aldag, A.W., and Vannice, M.A. (1970). On the slow uptake of hydrogen by platinized carbon. *J. Catalysis,* 18, 46-51.

2006[9]; Yang, 2006[10]). However, many questions remained unanswered, especially in respect with the energetics and dynamics of hydrogen on Pd-modified activated carbon fibers. This report provides new information aimed to clarification of the mechanism of enhanced hydrogen uptake in Pd-doped activated carbon fibers.

Experimental

Activated carbon fibers (ACF) were produced at Clemson University from an isotropic pitch precursor, as described elsewhere (Basova, 2004[11]). To obtain Pd-contained ACF, the pitch precursor was mixed prior to spinning with palladium acetylacetonate, Pd(acac)$_2$, at a Pd ratio corresponding to 1 wt% Pd. Carbon fibers (both Pd-free and Pd-containing) with various levels of activation (as measured by the burn-off degree) were obtained by activation in pure CO_2 following stabilization and carbonization. The Pd-free sample were designated as K-230-X, while the Pd-containing samples were designated as K-230-Pd-X, where X denotes the activation level expressed as the percentage burn-off achieved through thermal activation in CO_2. The Pd-free samples served as controls.

Using standard characterization by adsorption of N_2 at 77 K and of CO_2 at 273 K (Autosorb 1C from Quantachrome) it was determined that the BET surface area and the total pore volume increased as the burn-off degree after activation increased. A detailed analysis of pores size distribution was carried out by the DFT method applied to N_2 and CO_2 adsorption results. Characterization of Pd-containing fibers by scanning electron microscopy (SEM) revealed the presence of numerous highly dispersed Pd particles (~ 2 nm) as well as of larger particles (up to ~ 40 nm). Additional details on the physical properties of Pd-free and Pd-containing ACF are presented elsewhere (Basova, 2005; Gallego, 2006).

Hydrogen adsorption isotherms were measured using a microgravimetric system (IGA 01 from Hiden Isochema). All samples were outgased at 300 ºC prior to each H_2 adsorption runs. The sample weight was about 100 mg, and the experimental results were corrected for buoyancy effects related to the displacement of gas by the sample, sample holder, and pan. The dry sample density was calculated from helium adsorption measurements. Both adsorption equilibrium and adsorption kinetic data were collected from a series of runs at various temperatures (from 5 ºC to 80 ºC) in the pressure range of 0 – 2 MPa.

Results

Effect of CO_2 activation on surface area and porosity

Characterization of physical properties of carbon fibers activated at various levels of burn-off confirmed that CO_2 activation is an effective method for controlled development of internal porosity and expansion of internal BET surface area.
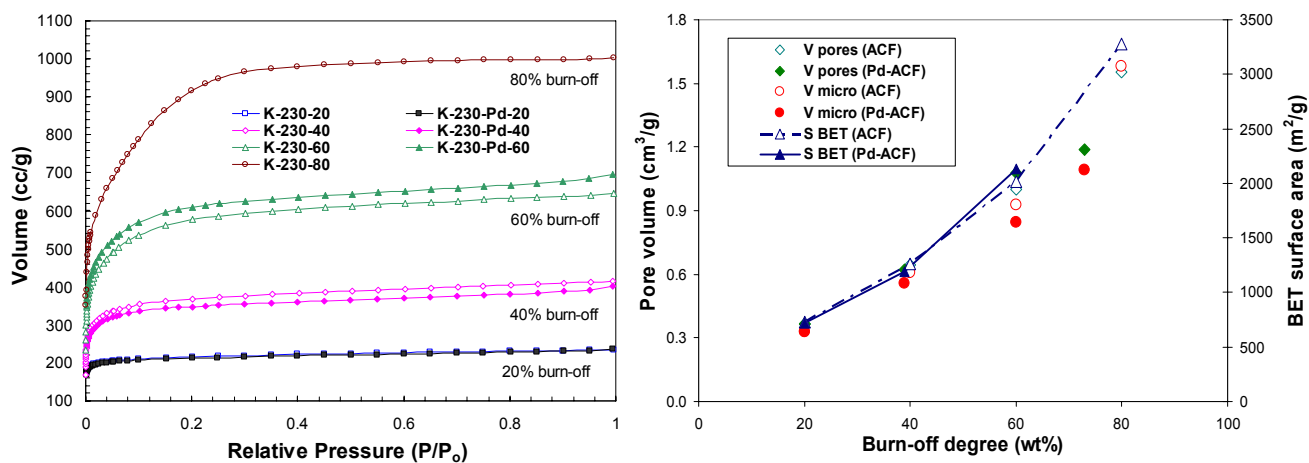
[7] Lueking, A., and Yang, R. T., (2004) Hydrogen spillover to enhance hydrogen storage – study of the effect of carbon physicochemical properties, *Appl. Catal. A: General*, 265, 259-268.

[8] Zacharia, R., Kim, K. Y., Kibria, A. K. M. F., Nahm, K. S. (2005) Enhancement of hydrogen storage capacity of carbon nanotubes via spillover form vanadium and palladium nanoparticles, *Chem. Phys. Letters*, 412, 369-375.

[9] Anson, A., Lafuente, E., Urriolabeitia, E., Navarro, R., Benito, A. M., Maser, W. K., Martinez, M. T. (2006) *J. Phys. Chem. B*, 110, 6643-6648.

[10] Yang, F. H., Lachawiec, A. J., Yang, R. T. (2006) Adsorption of spillover hydrogen atoms on single wall carbon nanotubes, *J. Phys. Chem. B*, 110, 6236-6244.

[11] Basova, Y. V., Edie D. D., Lee, Y. S., Reid, L. K., Ryu, S. K., (2004). Effect of precursor composition on the activation of pitch based carbon fibres, *Carbon*, 42, 485-495.

Figure 1: (a) N_2 adsorption isotherms at 77 K for Pd-free ACF and Pd-containing ACF at various levels of activation (expressed as burn-off degree); (b) variation of BET surface area and pore volume with the increase of activation level.

As **Fig. 1a** shows, the N_2 adsorption isotherms revealed little differences between Pd-free and Pd-containing ACF at equal activation levels, but large differences between samples with various levels of activation. All isotherms are of Type I, with practically no hysteresis, indicative of a dominant microporous character. The values of BET surface area and total pore volume increase almost linearly with the degree of burn-off (**Fig. 1b**); a similar dependence is seen for the micropore volume (from N_2 adsorption, based on DR method) and for the volume of ultramicropores (obtained from CO_2 adsorption). All characteristic structural data are summarized in **Table 1**.

Table 1. Measured values of BET surface area, total pore volume, and micropore volume of Pd-free and pd-modified activated carbon fibers at various levels of activation in CO_2

			Pd-free ACF		
BO degree	S_{BET}	$V_{total\ pores}$	$V_{\mu-pores\ (t\ method)}$	$V_{\mu-pores\ (DR)}$	$V_{\mu-pores(CO2)}$
%	m^2/g	cm^3/g	cm^3/g	cm^3/g	cm^3/g
20	730	0.364	0.304	0.331	0.243
40	1260	0.644	0.506	0.608	0.290
60	2020	0.999	0.765	0.927	0.319
80	3280	1.554	1.406	1.579	0.617

			Pd-containing ACF		
BO degree	S_{BET}	$V_{total\ pores}$	$V_{\mu-pores\ (t\ method)}$	$V_{\mu-pores\ (DR)}$	$V_{\mu-pores(CO2)}$
%	m^2/g	cm^3/g	cm^3/g	cm^3/g	cm^3/g
20	720	0.367	0.298	0.328	0.238
39	1192	0.622	0.475	0.558	0.296
60	2133	1.078	0.818	0.845	0.353
73	2295	1.189	0.851	1.091	

Notes: [a] from N_2 adsorption, based on t-method; [b] from N_2 adsorption, based on DR-method; [c] from CO_2 adsorption, d < 14 Å

The pore size distribution in the range of micropore sizes (3 – 14 Å) revealed by CO_2 adsorption at 273 K is shown in **Fig. 2a.** In the range of narrow micropores (pore sizes smaller than 7 Å) the distribution of porosity is only weakly affected by differences in the activation level. All samples show the narrow microporosity characteristic to most activated carbons, and gradually develop increasingly larger supermicroporosity (pore sizes between 7 and 20 Å) by activation at larger levels of burn-off. The increase of activation levels has a particularly strong effect on the pores with sizes at the border between the micropore and mesopore classes (20 – 30 Å). This is illustrated by the cumulative pore size distributions of **Fig. 2b** where the distributions calculated by the DFT method from CO_2 and N_2 adsorption data are combined on a common scale.
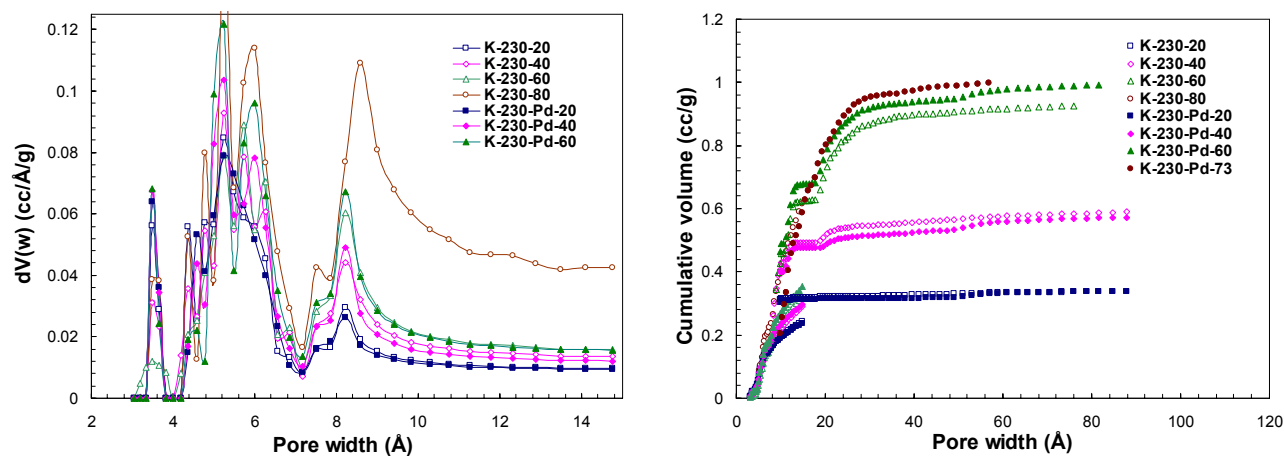
Figure 2: Pore size distributions calculated from CO_2 and N_2 adsorption using the DFT method and assuming slit-shaped pore for CO_2 calculations and slit-cylindrical shape for N_2 calculation.

Two important conclusions can be drawn from these results on the development of porosity and its relationship with the levels of activation by CO_2. First, is the evident that activation at high levels of burn-off, although effective in development of large BET surface areas, contributes very little to the increase of pore volumes in the range of narrow micropores (< 7 Å), which are better suited for physical adsorption of H_2 at low pressures. On the other hand, the growth of pore volumes corresponding to supermicropores and narrow mesopores (7 – 30 Å) may have a significant effect on the adsorption capacity at large pressures. Second, there is practically no difference in porosity and surface area characteristics between Pd-free ACF and Pd-modified ACF. This makes possible comparing hydrogen adsorption properties of samples with and without Pd at equal levels of burn-off. In other words, the specific contribution of Pd to the excess adsorption measured for Pd-containing samples can be isolated by simply subtracting adsorption on support, which is accurately identified with the adsorption measured for the corresponding Pd-free sample.

Hydrogen adsorption on Pd-free activated carbon fibers

Hydrogen adsorption isotherms were measured in a narrow range of temperatures (10 to 80 ºC) considered practical for operation of on board fuel cell devices. As explained before, the reference term for H_2 adsorption on every Pd-loaded ACF was the Pd-free ACF with a comparable activation level (burn-off degree).
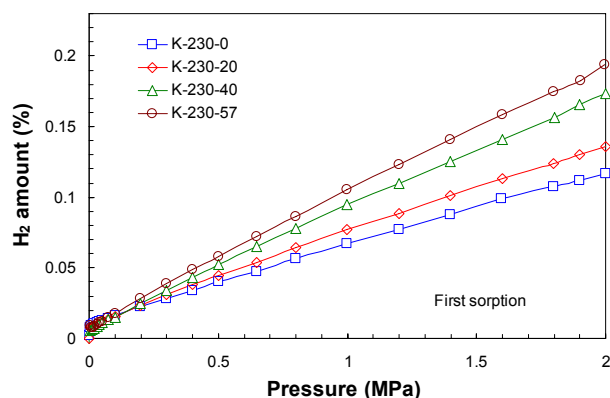

Figure 3: Hydrogen adsorption isotherms at 298 K on Pd-free activated carbon fibers with various levels of activation
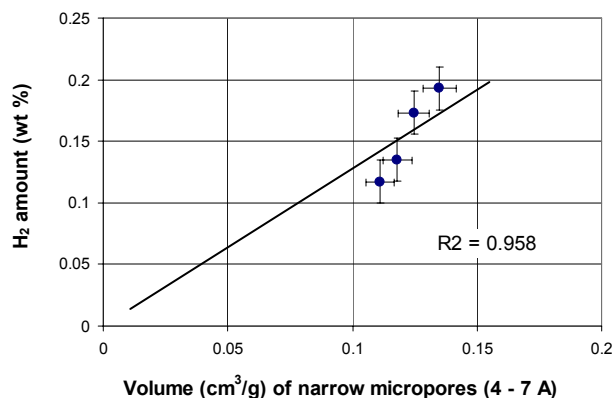
Figure 4: Linear correlation between amounts of H_2 adsorbed (at 298 K and 2 MPa) and the volume of narrow micropores between 4 and 7 Å

Fig. 3 shows excess adsorption isotherms for hydrogen measured at 25 ºC on Pd-free activated fibers with various levels of activation. In the pressure range studied (0 – 2 MPa) the isotherms are close to a linear shape; in other words, at 298 K and in this pressure range adsorption of hydrogen on activated carbons is still in the Henry region. This result is in agreement with many other reports on hydrogen adsorption on activated carbon materials, which show that at 298 K the curvature of adsorption isotherms occurs at pressures higher than 2 MPa (Anson, 2006[9]; de la Casa-Lillo, 2002[12]). On the other hand, the amounts adsorbed at the maximum pressure investigated in this study (2 MPa) increase with the increase of the activation level of Pd-free ACF. Searching for an empirical relationship between the amounts adsorbed at 2 MPa and various textural properties of activated carbon fibers, the best correlation was found with the volume of narrow micropores corresponding to the first significant maximum (approximatively 5 to 7 Å) found in the pore size distribution calculated by the NLDFT analysis of CO_2 adsorption data at 273 K (Fig. 3). This is not surprising, considering that the hypothetical reduced pressure of hydrogen at 298 K and 2 MPa (P/P_o = 0.0188) is in the range where adsorption in narrow micropores prevails; in this calculation, a hypothetical "saturation pressure" of hydrogen at 298 K (P_o = 106 MPa) was estimated using an empirical equation (Agarwal, 1988[13]). Using the same approach it was previously explained (Jorda-Beneyto, 2007[14]) why adsorption data at room temperature and moderate pressure (up to 20 MPa) correlate with the volume of narrow micropores, while data

[12] de la Casa-Lillo, M. A.; Lamari-Darkrim, F., Cazorla-Amoros, D., and Linares-Solano, A., Hydrogen storage in activated carbons and activated carbon fibers, *J. Phys. Chem B,* **2002**, *166* 10930-10934.

[13] Agarwal, R. K., Schwarz, J. A., Analysis of high-pressure adsorption of gases on activated carbon by potential-theory, Carbon **1988**, *26*, 873-887.

[14] Jorda-Beneyto, M., Suarez-Garcia, F., Lozano-Castello, D., Cazorla-Amoros, D., Linares-Solano, A., Hydrogen storage on chemically activated carbons abd carbon nanomaterials at high pressures, Carbon **2007**, *45*, 293-303.

at higher pressure (50 MPa) correlate better with total micropore volume (< 20 Å, from N_2 adsorption at 77 K). Similarly, the effect of narrow micropores is dominant for adsorption at 77 K and low pressures (0.1 MPa), while at higher pressure (10 – 20 MPa) contribution of wider microporosity becomes increasingly important (Texier-Mandoki, 2004[15]; Zhao, 2005[16]; Zhao 2006[17]).

Hydrogen adsorption on Pd-modified activated carbon fibers

Hydrogen adsorption on Pd-modified ACF was higher than on their Pd-free counterparts. This is shown in Fig. 4 for samples activated at 20% and 40% burn-off. Adsorption isotherms by Pd-free ACF with equal activation levels are shown for comparison. The increase in H_2 uptake, although not spectacular, is measurable and reproducible. The difference is larger than what would be expected based on formation of Pd hydride on contact with hydrogen. The dotted lines in Fig. 4 represent the expected adsorption calculated by summing the amounts measured for a Pd-free carbon support with an equal activation level, and the amount of hydrogen which would be bound in palladium hydride ($PdH_{0.6}$), based on the known Pd content of the samples. The difference between the actually measured adsorption amounts and the expected uptake is attributed to spilt over hydrogen. The spillover mechanism is, in essence, a combination of catalytic dissociation of molecular H_2 on catalytic sites (Pd) and surface diffusion of atomic H species, followed by their storage at remote storage sites on the carbon support, which otherwise were not accessible to direct adsorption of molecular H_2.
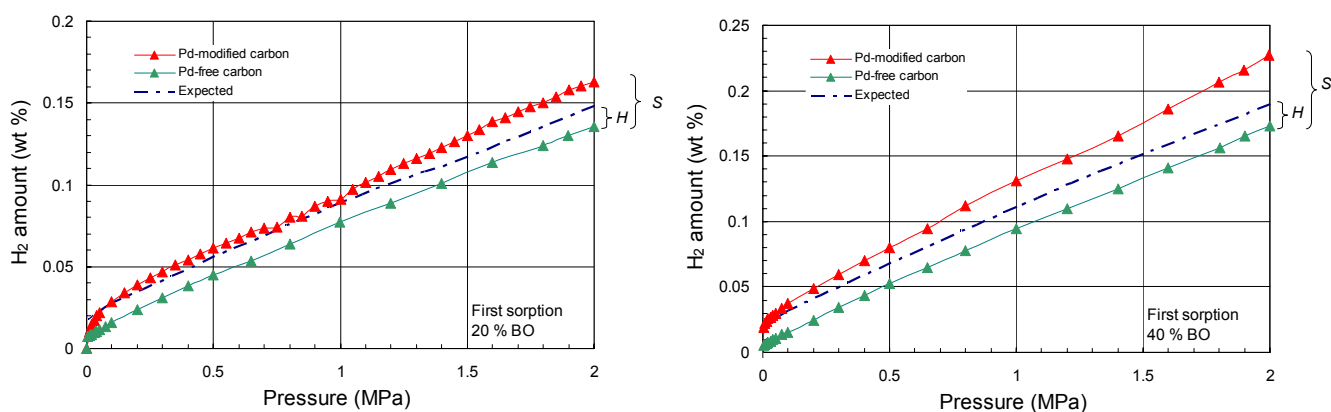

Figure 4: Excess hydrogen adsorption isotherms for Pd-free ACF and Pd-modified ACF for activation levels corresponding to 20% burn-off (a) and 40 % burn-off (b). The broken line represents the expected amounts adsorbed on Pd-modified ACF if all hydrogen were bound to carbon support plus Pd hydride. The difference S-H at the highest pressure investigated (2 MPa) is attributed to spilt-over hydrogen. The amount of Pd is 1.91 wt % (a) and 2.55 wt % (b). Calculations were made assuming 0.7 wt % H in saturated β-palladium hydride ($PdH_{0.6}$).

The effect of temperature on adsorption isotherms of Pd-containing fibers activated at 20 % and direct-activated at 40 % burn-off is illustrated in Fig. 5. Globally, an increase of temperature causes a decrease of adsorbed amounts over most of the pressure range investigated (0 to 20 bar). This is clearly seen in Figs. 5,a and 6, a and is the behavior expected for physical adsorption, which is exothermic. HEAT OF ADSORPTION ?? At a closer look, it is apparent that in the low pressure range (i.e. below 1 bar) the increase in temperature has the opposite effect: he higher the temperature, the higher are the amounts adsorbed, especially at the lowest end of the pressure scale (below 200 mbar). At the highest temperatures studied (60 and 80 ºC) the adsorption isotherms of both activated samples containing Pd show an abrupt initial adsorption of hydrogen, followed by a more or less flat segment at pressures higher than 300 – 400 mbar. The steep increase of the adsorption isotherm is less pronounced at lower temperatures (40 and 25 ºC). For the lowest temperatures studied (0 and 2 ºC) the isotherms are close to linear shape over the whole pressure range, thus resembling the shape of adsorption isotherms on bare carbon supports, Fig. 3.

The increase of the

[15] Texier-Mandoki, N., Dentzer, j., Piquero, T., Saadallah, S., David, P., and Vix-Guterl, C., Hydrogen storage in activated carbon materials: Role of the nanoporous texture, Carbon, **2004**, *42*, 2735-2777.

[16] Zhao, X. B., Xiao, B., Fletcher, A. J., Thomas, K. M., Hydrogen adsorption on functionalized nanoporous activated carbons, *J. Phys. Chem. B* **2005**, *109*, 8880-8888.

[17] Xhao, X., Villar-Rodil, S., Fletcher, A. J., Thomas, K. M., Kinetic isotope effect for H_2 and D_2 quantum moleculr sieving in adsorption/desorption on porous carbon materials, *J. Phys Chem. B* **2006**, *110*, 9947-9955.
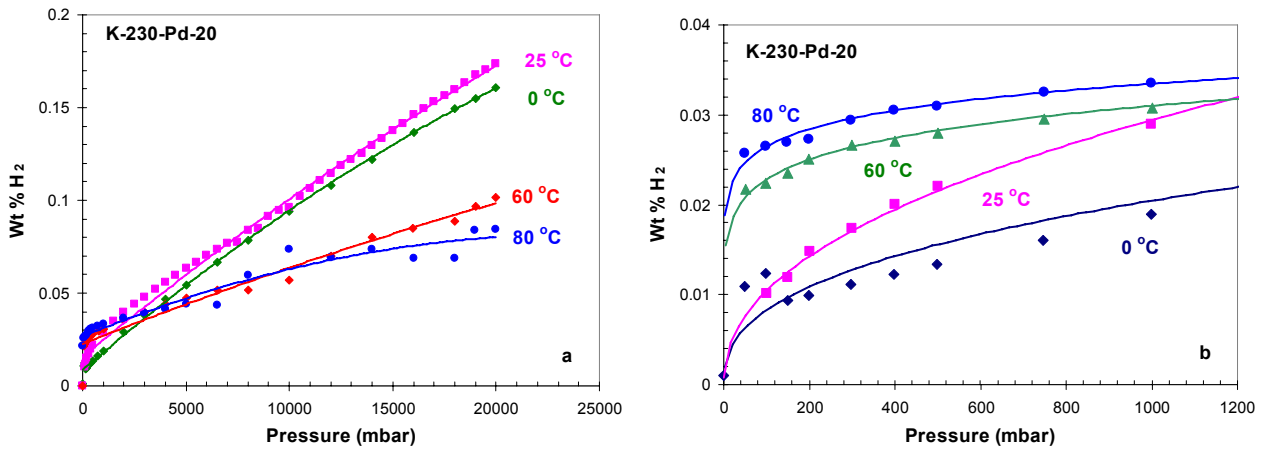
Figure 5: Effect of temperature on hydrogen adsorption isotherms for Pd-ACF samples activated at 20% burn-off: (a) full pressure range; (b) low pressure range. Solid lines were added as a helper to the eye.
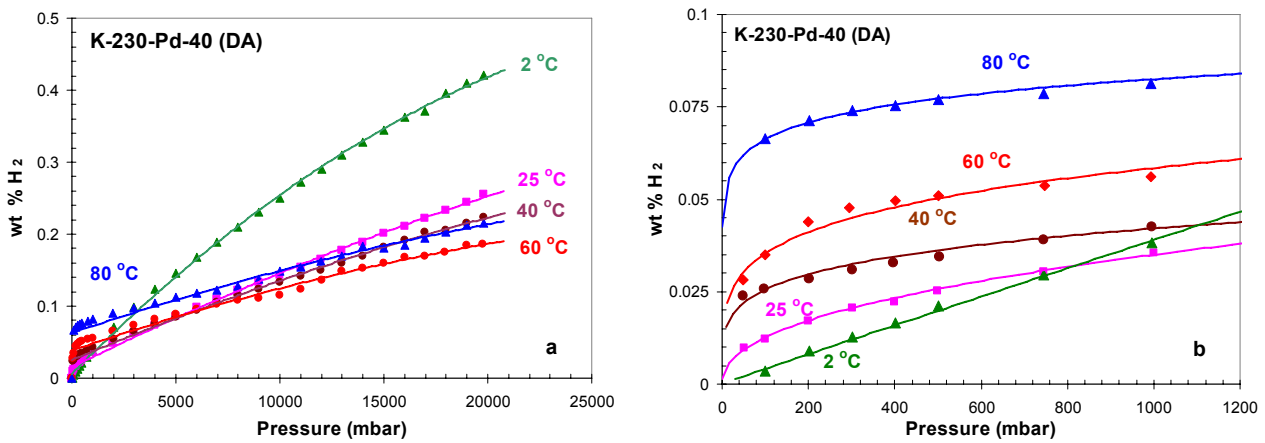

Figure 6: Effect of temperature on hydrogen adsorption isotherms for Pd-ACF samples direct activated at 40% burn-off: (a) full pressure range; (b) low pressure range. Solid lines were added as a helper to the eye.