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## Detection of Hydrogen Spillover in Palladium-Modified Activated Carbon Fibers during Hydrogen Adsorption

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Palladium-modified activated carbon fibers (Pd-ACF) are being evaluated for adsorptive hydrogen storage at near-ambient conditions because of their enhanced hydrogen uptake in comparison to Pd-free ACF. The net uptake enhancement (at room temperature and 2 MPa) is in excess of the amount corresponding to formation of  $\beta$ -Pd hydride and is usually attributed to hydrogen spillover. In this paper, inelastic neutron scattering was used to investigate the state of hydrogen in Pd-containing activated carbon fibers loaded at 77 K with 2.5 wt %  $H_2$ . It was found that new C–H bonds were formed, at the expense of physisorbed  $H_2$ , during prolonged in situ exposure to 1.6 MPa hydrogen at 20 °C. This finding is a postfactum proof of the atomic nature of H species formed in presence of a Pd catalyst and of their subsequent spillover and binding to the carbon support. Chemisorption of hydrogen may explain the reduction in hydrogen uptake from first to second adsorption cycle.

### Introduction

Enhancing the hydrogen sorption capacity of microporous carbon materials at near-ambient temperatures continues to be a subject of intense research. New high-capacity adsorbents are sought with hydrogen binding energies intermediate between physisorption and chemisorption.<sup>1,2</sup> In the late 80s, Schwarz pioneered the concept of adding small amounts of transition metals to activated carbons in order to increase their storage capacity through the hydrogen spillover mechanism.<sup>3</sup> Later, Lueking and Yang used the concept of spillover to explain the enhanced hydrogen uptake by multiwalled carbon nanotubes containing a small amount of residual catalyst<sup>4</sup> and designed a strategy for increasing the  $H_2$  capacity of microporous adsorbents.<sup>5</sup> Since then, numerous other examples of enhanced  $H_2$  uptake in presence of transition metal catalysts with nearly filled d shells (Pt, Pd, Ni) have been reported<sup>6–8</sup> and explained by the spillover mechanism. A comprehensive review of the subject has been published recently by Wang and Yang.<sup>9</sup>

Hydrogen spillover is a mechanism well documented for heterogeneous catalytic reactions<sup>10–14</sup> and is described as dissociative adsorption of  $H_2$  on metal catalyst particles, followed by migration of H atoms to the support and reaction at remote surface sites. However, direct proof of the mechanism is difficult to obtain. Detection of atomic hydrogen is a challenging task because measuring dynamics of H atoms on metal nanoparticles dispersed on adsorbents is difficult by traditional surface analysis techniques. Absorption of electromagnetic radiation by small metal particles and carbon materials limits the applicability of Raman and IR spectroscopy, and the electrical conductivity of carbon limits the use of magnetic resonance. In contrast, neutron vibrational spectroscopy is uniquely able to reveal the state of hydrogen and its dynamics

on carbon adsorbents and on carbon-supported metal nanoparticles.<sup>15</sup> Inelastic neutron scattering (INS) was instrumental to prove the atomic nature of spilt-over hydrogen species: prolonged exposure to hydrogen of carbon-supported fuel cell catalysts (containing Pd,<sup>16</sup> Pt, and Ru<sup>17</sup>) induced dissociation and slow transfer and binding of H atoms to the carbon support at room temperature. However, no direct evidence has been provided that a mechanism involving atomic H species is responsible for the enhanced  $H_2$  uptake measured experimentally<sup>4–8,18</sup> at near-ambient temperatures on carbon materials modified with group VIII metals. Moreover, it was suggested that hydrogen spillover might involve molecularly physisorbed  $H_2$  species released by small Pt clusters supported on carbon nanotubes.<sup>19</sup>

In a recent report, Campesi et al.<sup>18</sup> showed that the room-temperature hydrogen uptake capacity of ordered porous carbon containing Pd clusters was enhanced in comparison with the Pd-free material; however, the adsorption isotherms were not completely reversible. Very similar results were reported by Anson et al.<sup>20</sup> for activated carbon and carbon nanotubes modified with Pd. The authors suggested that the presence of Pd in their material induced the spillover process and that some of the spilt-over hydrogen have been chemically bonded to the carbon support, and therefore it would not desorb at temperatures below 250–300 °C.<sup>18,20</sup> In the present study, inelastic neutron scattering was used to demonstrate the formation of new C–H bonds in Pd-containing activated carbon fibers after exposure to hydrogen at 20 °C and 1.6 MPa. This finding was then interpreted as a postfactum proof of the atomic nature of H species formed in presence of a Pd catalyst and of their subsequent spillover to the carbon support. The reaction of some of the spilt-over H with unsaturated carbon atoms to form new C–H bonds could also explain the partial irreversibility of hydrogen adsorbed during the first cycle and the reduction of total hydrogen uptake during the second adsorption cycle compared to the first.

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**TABLE 1: Physical Properties of Pd-ACF and ACF Samples<sup>a</sup>**

sample	Pd content (wt %)	burn-off degree (%)	N <sub>2</sub> adsorption (77 K)			CO <sub>2</sub> adsorption (273 K)		
			$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_{\mu\text{p-DR}}$ (cm <sup>3</sup> /g)	$V_{\mu\text{p-t-plot}}$ (cm <sup>3</sup> /g)	$S_{\text{DR}}$ (m <sup>2</sup> /g)	$V_{\mu\text{p-DR}}$ (cm <sup>3</sup> /g)	$V_{\mu\text{p}<8\text{\AA}}(\text{NLDFT})$ (cm <sup>3</sup> /g)
ACF	0	41.4	2017	0.80	0.72	1497	0.52	0.30
Pd-ACF	2	40.9	1878	0.88	0.77	1586	0.55	0.31

<sup>a</sup>  $S_{\text{BET}}$  = BET surface area;  $V_{\mu\text{p-DR}}$  = volume of micropores (<2 nm) by Dubinin–Radushkevich method;  $V_{\mu\text{p-t-plot}}$  = volume of micropores (<2 nm) by t-method;  $V_{\mu\text{p}<8\text{\AA}}(\text{NLDFT})$  = volume of narrow micropores (<0.8 nm) from NLDFT method (Quantachrome software). All properties reported are expressed per gram of material (ACF or Pd-ACF).

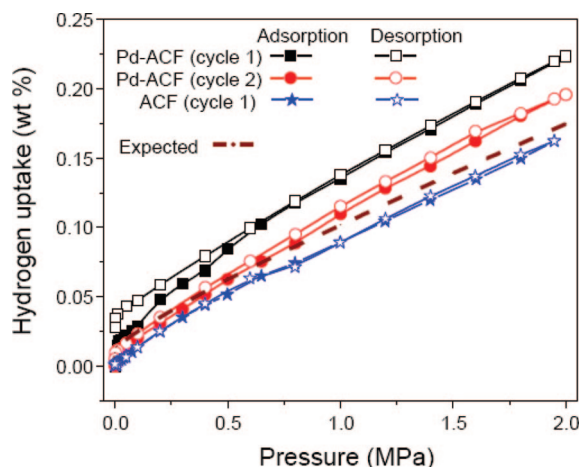
## Experimental Section

Palladium-containing and palladium-free activated carbon fibers (Pd-ACF and ACF) were produced from an isotropic petroleum pitch. For the Pd-ACF, the pitch was mixed with Pd acetylacetonate (1 wt % equivalent Pd) prior to melt spinning. The spun fibers were stabilized by slow oxidation in air (260 °C) and subsequently carbonized and activated at 900 °C under CO<sub>2</sub> in a single step (direct activation) to achieve a burnoff level of 40 – 45%.<sup>21</sup> The average fiber diameter for Pd-ACF and ACF was 15  $\mu\text{m}$ . The Pd content in the Pd-ACF after thermal treatment was 2 wt % Pd (measured by the combustion method), close to the result ( $1.6 \pm 0.2$  wt %) measured by prompt  $\gamma$  activation at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR). Additional details on the processing of ACF and Pd-ACF can be found in reference.<sup>22</sup> The physical properties of ACF and Pd-ACF samples are summarized in Table 1. Since Pd-ACF materials were prepared by mixing the Pd salt with the carbon precursor before carbonization and activation, it is not surprising that the micropore volume of Pd-ACF is very close to that of ACF. In fact, Wu et al. concluded in a related study<sup>22</sup> that the presence of Pd has no significant effect on the porosity development of pitch-based activated fibers obtained by this method. The rates of activation by CO<sub>2</sub> were however faster for Pd-ACF than for ACF, which demonstrates that Pd has catalytic effect on carbon oxidation by CO<sub>2</sub>.

Hydrogen adsorption isotherms were measured by the gravimetric method using IGA-1 microbalance from Hiden Isochema. To avoid all traces of condensable vapors that might affect gravimetric measurements, research-grade ultrahigh purity hydrogen (Matheson Gas, 99.9999%) was used, with the gas line passing through a bath of liquid nitrogen before entering the microbalance. Prior to exposure to hydrogen, samples of approximately ~100 mg were evacuated in situ at 300 °C for 8 h. Buoyancy corrections were made based on carbon skeleton density measured with a He pycnometer (Quantachrome).

INS studies were performed only on a Pd-ACF sample (mass, 0.9928 g) in order to investigate the effect of near-ambient temperature conditions on a sample with preadsorbed hydrogen, i.e., conditions favorable to hydrogen spillover. The INS spectra were used to identify the molecular rotational levels associated with physisorbed H<sub>2</sub> and the vibrational signature of chemisorbed hydrogen. The measurements were made using the filter-analyzer neutron spectrometer (FANS)<sup>23</sup> at the NCNR. The instrument is equipped with a combination of bismuth, beryllium, and graphite filter (resolution 1.2 meV) and with two different monochromators that were used interchangeably: pyrolytic graphite for the energy range of molecular rotors (6.2 to 25 meV) and copper for the energy range of lattice and chemical bonds vibrations (25–160 meV).<sup>24</sup>

Sample preparation prior to INS measurements was made to simulate the conditions utilized during gravimetric hydrogen adsorption measurements. The Pd-ACF sample was evacuated



**Figure 1.** Room-temperature hydrogen adsorption isotherms for ACF and Pd-ACF (2 wt % Pd). For clarity, only one adsorption–desorption cycle is shown for ACF, while two cycles are shown for Pd-ACF (adsorption, filled symbols; desorption, open symbols).

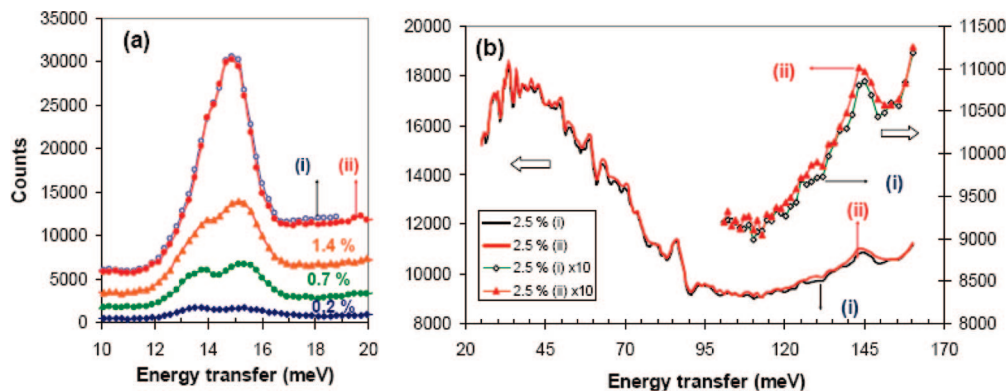
at 285 °C for 14 h at 1.3 Pa and transferred, in a moisture-free He atmosphere, to the aluminum sample holder of the FANS spectrometer, which was connected to a gas distribution manifold. The background spectrum of the pristine Pd-ACF sample under vacuum was collected, and subtracted from all subsequently measured spectra. All INS spectra were collected at 4 K.

## Results and Discussion

**Hydrogen Adsorption.** Hydrogen sorption isotherms for ACF and Pd-ACF measured at room temperature are shown in Figure 1. During the first cycle, Pd-ACF adsorbed 0.225 wt % hydrogen at 2 MPa, but only 90% of the adsorbed hydrogen was reversible during evacuation at room temperature. The adsorption capacity decreased down to 0.208 wt % at 2 MPa during the second cycle. The sample was outgassed at 300 °C for 8 h between cycles. In contrast, ACF adsorbed only 0.16 wt % hydrogen at 2 MPa, all of which was fully reversible; the same results were obtained in the second cycle.

When comparing the hydrogen uptake of ACF and Pd-ACF, it is noted that Pd-ACF has a higher capacity than ACF despite the fact that both samples have comparable surface area and porosity (see Table 1). If it is assumed that the carbon support in both materials has equal physisorption contribution derived from their surface properties, then the additional amount of hydrogen uptake in Pd-ACF can be attributed to the presence of Pd.

On the basis of the 2 wt % Pd in Pd-ACF and by assumption that all Pd were converted to  $\beta$ -PdH<sub>0.7</sub>, the expected amount of hydrogen uptake caused by hydride formation was calculated and added to the contribution measured for the bare carbon support in ACF. The resultant values are shown as a dotted line in Figure 1. The net adsorption, i.e., the amount adsorbed



**Figure 2.** INS of Pd-ACF upon interaction with hydrogen. Rotational spectra (a) were measured at increasing amounts of  $\text{H}_2$  adsorbed at 77 K ( $\text{H}_2$  wt % shown on the curves). Rotational spectra (a) and vibrational spectra (b) recorded before and after thermal treatment for 24 h at 20 °C of the sample loaded with 2.5 wt %  $\text{H}_2$  at 77 K are marked, respectively, as (i) and (ii). A selected range of vibrational spectra is shown at 10 $\times$  magnification on the second ordinate in (b).

on Pd-ACF in excess of the amounts contributed by ACF and Pd hydride, can be regarded as the result of spilt-over hydrogen that resides on the carbon support in Pd-ACF. The decrease in the hydrogen uptake capacity of Pd-ACF in the second sorption cycle indicates that some of the spilt-over hydrogen is not completely reversible by evacuation at 300 °C.

**INS.** The Pd-ACF sample used for INS measurements was not previously exposed to hydrogen and was prepared for testing as described above. The test was conducted in two phases. First, the sample was dosed with hydrogen at 77 K to investigate the state of physically adsorbed hydrogen. The amounts adsorbed after each dose were calculated from pressure changes in the gas manifold and the known dosing volume. Once equilibrium was reached at 77 K for each hydrogen dose, the sample was cooled down to 4 K and a spectrum was collected using the graphite monochromator (energy transfer range 6–25 meV). This procedure was repeated at increasing hydrogen loadings: 0.2, 0.7, 1.4, and 2.5 wt % (adsorbed at 77 K). When the hydrogen loading reached 2.5 wt %, a full INS spectrum was collected using both graphite and copper monochromators. The collected spectra are shown in Figure 2.

Over the energy transfer range shown in Figure 2a, neutron scattering probes transitions between rotational states  $J = 0 \rightarrow 1$  (para  $\rightarrow$  ortho) of molecular  $\text{H}_2$ , where the energy of a given rotational state,  $J$ , is  $BJ(J+1)$  for a freely rotating  $\text{H}_2$  with  $B$  being the rotational constant of 7.35 meV.<sup>25</sup> The rotational peak, which increases with  $\text{H}_2$  loading, is split asymmetrically with components at 13.8–14 meV and 15.0–15.5 meV. Such splitting, which has been previously reported for physisorbed  $\text{H}_2$ , indicates that rotation of  $\text{H}_2$  molecules adsorbed in carbon micropores is hindered compared to solid  $\text{H}_2$ .<sup>25,26</sup>

In the second stage, a thermal treatment was applied to the sample loaded with 2.5 wt %  $\text{H}_2$ , in order to stimulate spillover. With the sample tube isolated from the gas manifold, the sample was warmed up to  $\sim 20$  °C. This caused significant desorption of physisorbed hydrogen and led to an estimated increase of hydrogen pressure up to 1.6 MPa inside the sample tube. The sample was kept at these conditions for 24 h, allowing spillover to occur and the spilt-over hydrogen to occupy the energetically favorable sites. After 24 h, the sample was cooled down to 4 K and the INS spectrum after the thermal treatment was collected using both monochromators (Figures 2a and 2b).

The test mimicking spillover conditions produced small changes in the spectra. On the basis of information from adsorption isotherms (Figure 1), it is estimated that only  $\sim 2\%$  of the amount of hydrogen loaded by physical adsorption at 77

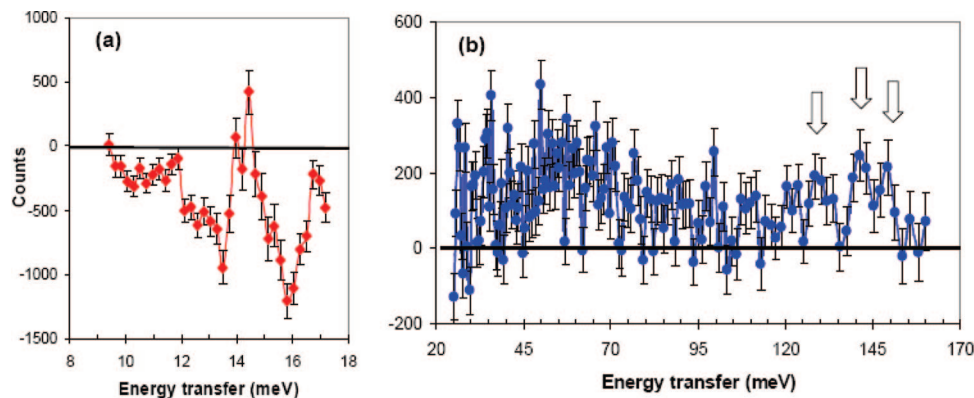
K remained in the adsorbed state on Pd-ACF during thermal treatment. The fraction of  $\text{H}_2$  molecules available for spillover was even smaller, about 1.2% of all  $\text{H}_2$  in the sample tube. About 98% of hydrogen went into the gas phase in conditions of thermal treatment (20 °C and 1.6 MPa). Readsorption of gas phase  $\text{H}_2$  on cooling (to collect INS spectra) produced physisorbed states, essentially indistinguishable from those existing before thermal treatment. This explains why the change in the INS spectra induced by thermal treatment is that small (Figure 2b). However, they are related to the change in the state of hydrogen adsorbed on Pd-ACF during thermal treatment.

Figure 3 shows the difference spectra (“after treatment” minus “before treatment”) in the two energy ranges defined by the differing monochromators. In the low energy transfer range, the difference spectrum has negative lobes (Figure 3a), while it is positive in the high energy transfer range (Figure 3b). The drop in intensity of rotational spectrum suggests that some loss of hydrogen molecules occurred from molecularly physisorbed states. In the energy range where neutron spectra reveal vibrational modes of hydrogen bonded to the matrix of Pd-ACF, the difference plot (Figure 3b) shows two distinct regions (40–100 meV and 100–160 meV) of enhanced intensity after thermal treatment. The gain in intensity indicates an increase in the population of chemisorbed hydrogen after thermal treatment and is discussed below.

Albers et al.<sup>27</sup> measured INS spectra of Pd/carbon catalysts (20 wt % Pd) and pure Pd exposed to hydrogen at room temperature. They identified a peak at 59–61 meV and an asymmetric tail at 70–100 meV caused by formation of  $\beta\text{-PdH}_x$ . These features are also observed for Pd-ACF (Figure 3b), but they are overlapped with a broad band with a maximum at  $\sim 50$  meV, caused by molecular recoil. On the other hand, INS spectra of disordered carbon materials<sup>24,28,29</sup> exhibit inelastic peaks below 90 meV that originate in vibrations of the carbon skeleton, and peaks above 90 meV that are caused by C–H vibrations. On the basis of theoretical calculations on typical model compounds, the latter have been identified as out-of-plane (about 95–110 meV) and in-plane (about 120–180 meV) bending modes of terminal H atoms bonded to  $\text{sp}^2$  carbon atoms in aromatic polycyclic structures.<sup>24,29</sup>

On the basis of this information, several peaks in Figure 3b (at energy levels 128, 141, and 149 meV) could potentially arise from in-plane C–H bending vibrations. Their FWHM is larger than the instrument resolution at these energy transfers. The development of these new features coincides with the decrease in intensity of the rotational peak. Apparently, a fraction of





**Figure 3.** Difference INS spectra showing changes produced by thermal treatment at 20 °C of a Pd-ACF sample preloaded with 2.5 wt % H<sub>2</sub> at 77 K. The negative difference in (a) shows the loss of molecularly physisorbed H<sub>2</sub>. The positive difference in (b) shows formation of new C–H bonds (arrows) and other features associated with Pd hydride and vibrations of carbon skeleton. Error bars are commensurate with counting statistics, indicating one standard deviation.

molecularly adsorbed H<sub>2</sub> was dissociated during thermal treatment, and spilt-over H atoms became bonded to unsaturated carbon atoms at edge sites of graphene structures.

Direct hydrogenation of unsaturated bonds in carbon is not likely at 20 °C. Noncatalytic hydrogenation of graphite is possible through direct reaction with hydrogen gas, but it requires high pressure (35 MPa) and temperature (350 °C).<sup>28</sup> On the other hand, direct hydrogenation of graphite and coal at room temperature has been observed only after extensive milling in hydrogen<sup>29,30</sup> or in reactive solvents.<sup>31</sup> The development of new INS peaks corresponding to C–H bonds at the experimental conditions used here (Figure 3b) indicates that atomic spilt-over hydrogen was present during thermal treatment and that it reacted with unsaturated carbon atoms, most probably at edge site positions of graphene sheets.

Hydrogen is adsorbed as atoms on surface of Pd particles and is dissolved interstitially in the Pd lattice to form two hydride phases. Formation of Pd hydride is not expected during initial loading with hydrogen at 77 K because of slow diffusion of hydrogen at low temperatures, but at 20 °C the  $\beta$ -PdH<sub>x</sub> ( $x \approx 0.7$ ) phase is stable and develops quickly. This H-rich  $\beta$  hydride phase acts as a “reservoir” of H atoms, and the carbon surface acts as a “pump”<sup>32</sup> that causes spilling of H atoms from fully saturated hydride particles.<sup>33</sup> The spillover process is a multistep dynamic process, most probably under kinetic control, rather than at thermodynamic equilibrium.<sup>33</sup> By use of in situ high-pressure XRD analysis, Bhat et al. have shown that the destabilizing action of the carbon support on the  $\beta$ -PdH<sub>x</sub> phase scales up with the increase of Pd-carbon contacts and with the temperature of pretreatment prior to H<sub>2</sub> adsorption.<sup>32</sup>

The possibility of facile transfer of H atoms between small metal clusters (Pt) and graphene has been theoretically analyzed in a recent study by Cheng et al.<sup>34</sup> Their study suggests that H atoms may subsist on graphene sheets either in weakly bonded physisorbed states or in strongly bonded chemisorbed states. The existence of atomic hydrogen in physisorbed states has been predicted theoretically<sup>35,36</sup> but is difficult to detect experimentally. If sufficiently stable, physisorbed H may experience surface diffusion and later recombination in some remote micropores that might be less accessible for direct adsorption from the gas phase. This would result in more molecular H<sub>2</sub> physisorbed on carbon. Alternatively, mobile H atoms in physisorbed states may reach strong binding sites on remote carbon atoms, forming either pairs<sup>37</sup> or collectively stabilized clusters<sup>38</sup> chemisorbed on graphene. Effectively, spilt-over hydrogen is trapped on the carbon support. In an experimental

study, Bhat et al.<sup>32</sup> have shown the influence of hydrogen trapping on phase transitions in palladium hydride supported on Pd-ACF. The results indirectly suggest that increasing the number of hydrogen trapping sites on the carbon support helps to “pump” hydrogen out of palladium hydride. On the basis of theoretical predictions and experimental results, it can be hypothesized that the excess hydrogen uptake capacity in Pd-ACF is due to trapping of spilt-over hydrogen in both chemisorbed and molecularly physisorbed forms. Since physisorbed hydrogen is weakly bonded, it is safe to assume that this hydrogen could be desorbed easily by evacuation at room temperature, while chemisorbed hydrogen require evacuation at high temperature as previously reported in the Pd-carbon system.<sup>18,20</sup> As a result, only physisorbed hydrogen may desorb after the first adsorption cycle, leaving chemisorbed hydrogen bonded on carbon. When the sample is exposed to hydrogen again, hydrogen could only be physisorbed, since all the chemisorption sites are already occupied. This is possibly the reason for the reduction in the adsorption capacity that is observed in the second cycle.

## Conclusion

This study revealed that C–H bonds were formed on the carbon support, at the expense of physisorbed hydrogen molecules, after exposing Pd-ACF preloaded with physisorbed H<sub>2</sub> to conditions favorable for hydrogen spillover. The chemisorbed hydrogen, which cannot be desorbed even after outgasing at 300 °C, explains the reduction in hydrogen uptake capacity from the first to the second adsorption cycle. It appears, however, that spillover leading to irreversible chemisorption in the system investigated here is of secondary importance compared to physisorption of molecular hydrogen, which accounts for a large part of enhanced uptake at 20 MPa and 25 °C.

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