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PALLADIUM-DOPED NANOPOROUS CARBON FIBERS FOR HYDROGEN STORAGE

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Abstract

Pd-free and Pd-containing activated carbon fibers (Pd-ACF) were synthesized from isotropic pitch. The source of Pd was a palladium salt that was premixed with pitch before fiber spinning and carbonization. Hydrogen adsorption was measured at near-ambient temperatures (5 to 80 ^{o}C) and moderate pressures (up to 20 bar). It was found that adsorption on Pd-ACF is always higher than that on corresponding ACF without Pd, and in excess of what it would be expected based solely on formation of Pd hydride. Additional characterization provided arguments in support of the hydrogen spillover mechanism. It was also found that temperature and pressure have opposite effects on physisorption and spillover. It was hypothesized that a narrow temperature range exists, where the kinetic advantage of H_2 spillover in Pd-ACF overlaps synergistically with the thermodynamic advantage of physisorption, thus contributing to enhanced uptakes compared with the Pd-free carbons.

Introduction

The hydrogen storage capacity of materials with high surface area and microporosity comes close to most of the DOE target levels, but only at cryogenic temperatures. High-surface area carbon-based materials are attractive for hydrogen storage because of their light weight, high stability, and low cost. However, the weak adsorption energy of hydrogen on most carbon materials (about 5 – 7 kJ/mol) limits the storage capacity at room temperature. Enhancing H_2 interaction with solid adsorbents at temperatures higher than the critical point of hydrogen (30 K) is a challenge when adsorption is caused by van der Waals forces only. Theoretical modeling has predicted that the uptake is enhanced if hydrogen is confined in maicropores with molecular dimensions.

Another route to enhance adsorption is by adding metals to nanostructured carbons. It was theoretically predicted that isolated transition metal atoms (Sc, Ti, V, Pt, Pd, etc) stabilized on sp^2-hybridized carbons (nanotubes, fullerenes, graphenes etc) induce multiple bonding of molecular H_2 with adsorption energies intermediate between physisorption and chemisorption [1,2]. However, this mechanism (known as Kubas chemistry) has not been proven experimentally due to the difficulty of stabilizing isolated single atoms of most transition metals. A second, more frequently reported route to enhanced uptake is the spillover mechanism [3]. It is based on the known property of nanoparticles of several transition metals to providie atomic hydrogen available for catalytic hydrogenation on remote surface sites. This mechanism may explain hydrogen uptakes larger than what can be normally attributed to chemisorption on exposed surface of metal nanoparticles or hydrogen dissolution and formation of bulk metal hydrides (in the case of Pd).

The work at Oak Ridge National Laboratory is focused on understanding the mechanism of metal-assisted hydrogen storage at near-ambient temperatures. It was found that the storage capacity of a multitude of carbon materials (commercial activated carbons, activated carbon fibers (ACF) and composites, single wall carbon nanotubes) is not higher than 0.2 – 0.3 wt% at 20 bar [4]. However, addition of small amounts of Pd to ACF caused a constant increase of hydrogen capacities [5]. It was also found out that the processing conditions of Pd-ACF control both the surface properties of the carbon support and the phase composition and dispersion of supported Pd particles [6]. This communication aims to further clarify the mechanism of enhanced hydrogen uptake in Pd-doped activated carbon fibers.

Experimental

Activated carbon fibers (ACF) of about 10 μm in diameter were synthesized from an isotropic pitch precursor [6]. A palladium salt (Pd-acetylacetonate) which was premixed with pitch before spinning was the source of Pd for Pd-modified fibers (Pd-ACF). All fibers (with and without Pd) were oxidative-stabilized, carbonized, and physically activated (with CO_2) to various levels of burn-off. The content of Pd in Pd-ACF was about 1.6 - 2.5 wt % after carbonization and activation. In an attempt to minimize the sintering of Pd during high temperature treatments, the steps of carbonization and activation were combined in a single process conducted under CO_2. This treatment was shown to improve the surface area and micropore volume of directly-activated samples in comparison with samples obtained through the two-step process at similar burn-off levels [7].

All ACF and Pd-ACF samples were characterized by N_2 adsorption at 77 K and CO_2 adsorption at 273 K using the Autosorb 1C instrument (Quantachrome). Structural characterization by in-situ high-pressure X-ray diffraction (up to 10 bar H_2) was done using the PANalytical X'Pert system and an Anthon Parr XRK 900 chamber with CuKα radiation. Hydrogen adsorption isotherms were measured microgravimetrically up to 20 bar H_2 using the IGA-01 system (Hiden Analytical) coupled with gas analysis by mass spectrometry. High-resolution aberration-corrected scanning transmission electron microscopy (STEM) was used to characterize the morphology of Pd nanoparaticles supported on carbon and of the microstructure of the neighboring carbon matrix. The dynamics of hydrogen adsorbed on Pd-ACF was characterized by inelastic neutron spectroscopy (INS) at NIST Center of Neutron Research in Gaithersburg, MD.

Results and Discussion

Enhanced hydrogen adsorption of Pd-ACF

Adsorption isotherms at 25 °C on Pd-free ACF with various levels of activation are shown in Fig. 1 [8]. The uptake capacity increases with the level of activation. The capacity increase correlates better with the volume of narrow micropores (< 7Å) obtained from DFT analysis of CO_2 adsorption than with the BET surface area or the total micropore volume calculated from N_2 adsorption data using the DR method. This trend reflects molecular properties of H_2. As expected, adsorption at 25 °C is dominated by physisorption in narrow micropores of carbon in both ACF and Pd-ACF. The isosteric heat of adsorption measured between 2 and 80 °C and 0.05 – 0.15 wt % H_2 is 7.5 – 9.6 kJ/mol (exothermic).

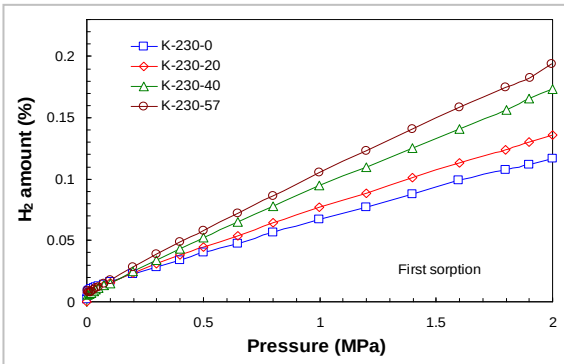

Figure 1. Excess hydrogen adsorption isotherms at 25 °C for Pd-free ACF physically activated at various levels of burn-off. Adapted after Ref. [8]

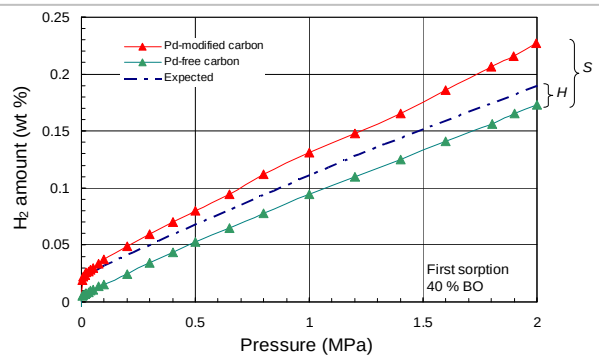

Figure 2. Excess hydrogen adsorption isotherms for Pd-free ACF and Pd-modified ACF (2.55 wt % Pd). Adapted after Ref. [8].

Adsorption on Pd-ACF was always higher than on their Pd-free counterparts. Figure 2 shows an example for samples activated at 40 % burn-off. The increase in H_2 uptake is reproducible. The dotted line in Fig. 2

is calculated additively from the amount measured for a Pd-free ACF with an equal level of activation, and the amount of hydrogen that would be required to convert all Pd in the sample to H-saturated Pd-hydride (β-$PdH_{0.66}$). The measured adsorption is larger than the calculated result, and the increase cannot be attributed solely to formation of Pd hydride. In the hydrogen storage literature such an enhanced uptake (Δ = S-H in Fig. 2) has been attributed to hydrogen spillover [3]. However, this mechanism is poorly understood and its direct evidence has been difficult to obtain.

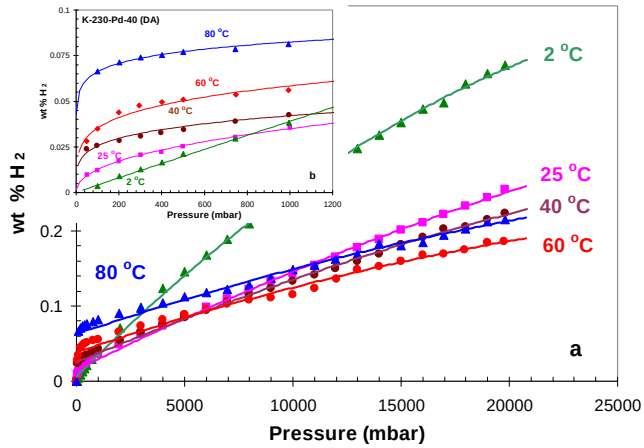

Figure 4. Effect of temperature on hydrogen adsorption isotherms for Pd-ACF samples direct activated at 40% burn-off: (a) full pressure range; (inset: low pressure range). Solid lines were drawn as a helper to the eye. Adapted after Ref. [8]

It was also found that temperature has an unusual effect on adsorption isotherms of H_2 on Pd-ACF, as illustrated in Fig. 3 for Pd-ACF direct-activated to 40 % burn-off. At pressures higher than ~ 200 mbar an increase in temperature causes a decrease of uptake, as expected for physisorption (exothermic). However, at pressures below ~ 200 mbar the effect of temperature is reversed, with higher initial adsorptions at higher temperatures (inset in Fig. 3). This unusual variation is observed in the range of pressures and temperatures where the two phases of Pd hydride (α-$PdH_{0.02}$ and β-$PdH_{0.66}$) are in equilibrium. Clearly, in a limited range of pressures and temperatures adsorption of H_2 occurs by a mechanism other than physisorption.

The unusual temperature effect may be caused by kinetic limitations in a pseudoequlibrium process; in this case at least one elementary step in the spillover cascade should be kinetically activated (e.g. surface diffusion of H atoms). However, assuming that all data are at equilibrium, the temperature effect indicates an endothermic process with a positive enthalpy change as large as 25 kJ/mol at < 200 mbar and < 0.05 wt% H_2. This process can possibly be identified with the exothermic release of H atoms from a saturated β-$PdH_{0.66}$ phase ($\Delta H^{formation}$ = - 36 kJ/mol). In either case, Pd hydride acts as a source of H atoms in a limited range of pressures (<200 mbar) and temperatures (20 - 80 ^oC).

Phase transformations in Pd particles supported on carbon

The structural changes induced by exposing ACF and Pd-ACF to high pressure (up to 10 bar) hydrogen were monitored using in-situ XRD measurements [9]. No changes were detected in the carbon structure after adsorption and desorption cycles at room temperature; however the equilibria between α and β phases of Pd hydride were easily monitored. Figure 4a shows the position and relative intensity of (111) peaks of the two phases as a function of partial pressure of H_2 in mixtures with He. The degree of $\beta \rightarrow \alpha$ conversion during desorption of hydrogen from 10 bar H_2 is plotted in Fig. 4b as a function of partial pressure of H_2. For comparison, also shown are similar plots for a reference Pd sponge sample and a commercial Pd on activated carbon catalyst (1% wt Pd from Acros Organics). The average size of Pd particles was 47.5 nm in Pd-ACF, 32.5 nm in Pd sponge, and 4.0 nm in the Pd catalyst.

The hydrogen pressure corresponding to 50 % $\beta \rightarrow \alpha$ conversion reflects the stability of the H-rich β-Pd hydride phase. The results show that the decomposition of β-Pd hydride during hydrogen desorption occurs earlier (at a higher pressure) on Pd-ACF in comparison with Pd-sponge and Pd catalyst. This shows that the H-rich Pd hydride phase on Pd-ACF is destabilized by the intimate contact with the activated carbon in Pd-ACF, which has hydrogen adsorption properties by itself. This is indirect evidence that the highly microporous carbon support in Pd-ACF acts like a “hydrogen pump” that causes “leaking” of H

atoms from the H-rich Pd hydride phase, as suggested for hydrogen spillover [10]. The higher "pumping efficiency" of the microporous carbon in Pd-ACF is probably the consequence of the preparation method of this material: premixing the Pd salt with the carbon precursor *before* carbonization produced Pd particles embedded in the carbon matrix with a better metal-carbon contact. In contrast, a less efficient metal-carbon contact is expected when Pd is added *after* formation of the carbon support (the case of Pd catalyst). These differences are reflected in the order of H_2 pressures that that correspond to a 50 % conversion of $\beta \rightarrow \alpha$ hydride phases: 5 mbar for Pd-ACF, 0.5 mbar for Pd catalyst, and 0.01 mbar for Pd sponge.

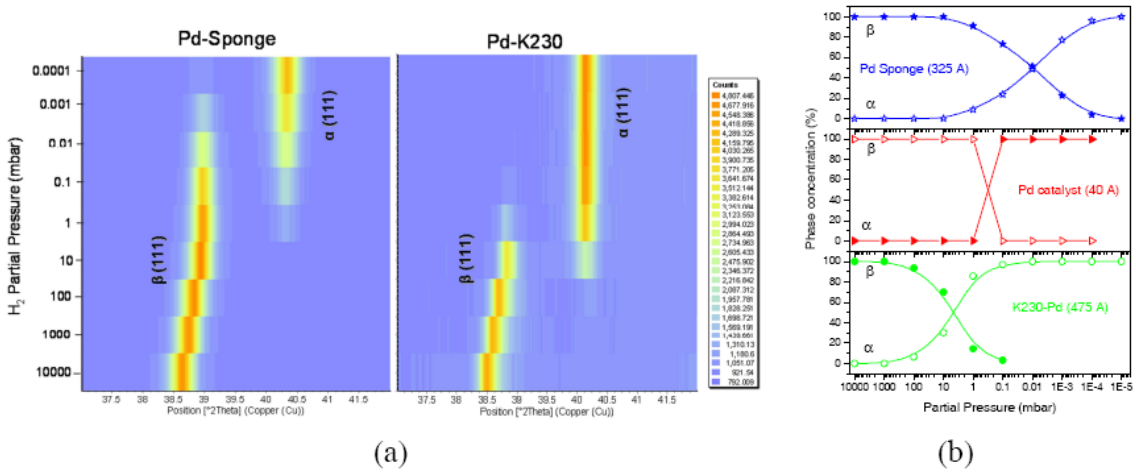

Figure 4: (a) XRD patterns of Pd-sponge and Pd-ACF under different hydrogen partial pressures; (b) degree of $\beta \rightarrow \alpha$ conversion of Pd hydride phases as a function of H_2 pressure. Adapted after Ref. [9].

The spillover mechanism

Based on surface characterization, there are very little differences in porosity and BET surface area characteristics between Pd-free ACF and Pd-modified ACF at equal levels of activation. This makes it possible quantifying the specific contribution of Pd to the hydrogen uptake of Pd-ACF by simply subtracting the uptake on a Pd-free ACF with an equal level of activation. In the hydrogen storage literature, any excess uptake (compared to the metal-free support) larger than what is expected from chemisorption on metal or from formation of a hydride phase is attributed to hydrogen spillover [3,10]. This is, in essence, a cascade of elementary steps comprising catalytic dissociation of molecular H_2 on metal sites (Pd), surface diffusion of atomic H across the metal-carbon interface, and storage at remote sites on carbon that otherwise might not be accessible to direct adsorption of molecular H_2. This complex process is very difficult to quantify. However, based on indirect evidence discussed above, it appears that the Pd hydride phase is a key player in the mechanism.

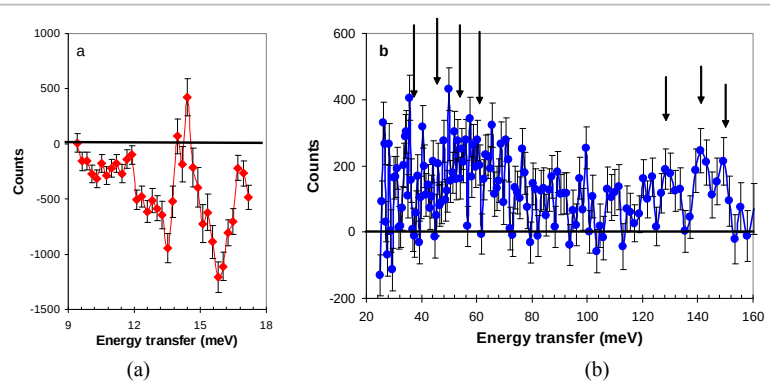

Figure 5. Difference INS spectra recorded after thermally cycling the Pd-ACF under a hydrogen atmosphere: (a) changes in rotational spectrum of physisorbed H_2; (b) changes in vibrational spectrum indicating development of Pd hydride (long arrows) and of new C-H bonds (short arrows).

Additional confirmation supporting the spillover mechanism was obtained from inelastic neutron spectroscopy (INS) tests on the FANS spectrometer at NIST Center for Neutron Research. All spectra were recorded at 4 K. A fresh Pd-ACF sample outgased in vacuum at 300 ^{o}C was loaded with 2.5 wt% H_2 at 77 K. The presence of molecular H_2 confined in carbon micropores was identified from the characteristic rotational spectrum at 14.7 meV [11]. After adsorption at 77 K, the sample was exposed to ~20 ^{o}C in a closed system, which caused an increase in pressure up to 17 bar. After 24 hr the sample was cooled back to 4 K and a second INS spectrum was recorded. Figure 5 shows the *changes* induced by thermal cycling. The difference spectra are negative in the low energy range characteristic for physisorbed H_2 (Fig. 5a), and positive in the energy range characteristic to phonon excitation of H in Pd hydride [12] and of out-of-plane vibrations of C-H bonds (Fig. 5b) [13]. The latter suggests that dangling bonds that might still exist at the edge carbon sites of graphene structures before thermal cycling were hydrogenated during exposure to ~20 ^{o}C in hydrogen. Since non-catalytic hydrogenation of carbon requires more severe pressure and temperature conditions, the intensification of C-H vibrations observed here indicates that active species, such as mobile H atoms, were present during thermal cycling. The test was repeated after outgasing the sample at 250 ^{o}C. Significantly, in the second cycle INS spectra showed no differences before and after exposure to 65 ^{o}C for 24 hr in a closed cell. The outgasing temperature was too low for breaking C-H bonds. However, all physically adsorbed hydrogen was quickly pumped out at 77–100 K at the end of the test.

Intensification of C-H vibrations is indirect proof of presence of mobile H atoms. Based on changes observed in the spectra, the extent to which hydrogenation of carbon occurs through H spillover is minor. The contribution of physical adsorption on the microporous support is dominant even on Pd-ACF. Recombination of spilt-over H atoms is more probable than binding to unsaturated C atoms. Hydrogenation of carbon by spilt-over H is undesirable because this form of hydrogen is strongly bound and desorption is more difficult.

Molecular bonding mechanism

Figure 6 shows aberration-corrected high-resolution scanning transmission electron microscopy (STEM) pictures of Pd-ACF [14]. The images were recorded simultaneously with pixel-to-pixel correlation in bright field (BF) and annular dark field (ADF) modes. The bright spots circled in the ADF image are isolated single Pd atoms stabilized in the carbon matrix. These atoms survived high temperature treatments (up to 860 ^{o}C) during carbonization and activation of Pd-ACF. It appears that the synthesis method selected, where a Pd salt was premixed with pitch *before* carbonization, was effective in preserving atomic dispersion for a fraction of total palladium present (although sintering and growth of larger particles occurs in parallel with another fraction of palladium). Due to its electronic structure with filled d^{10} shell, palladium is more resistant to sintering than, e.g. platinum.

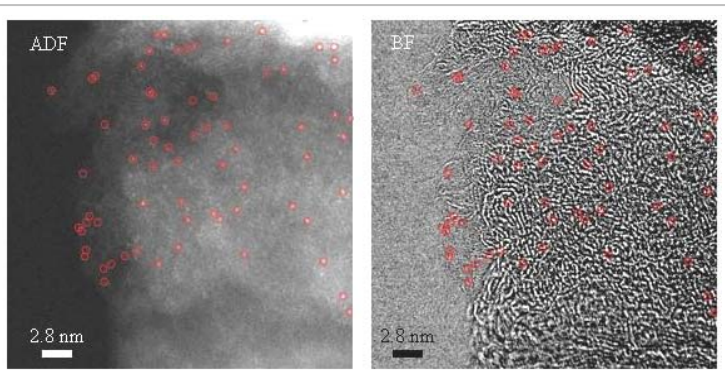

Figure 6. Pair of annular dark field (ADF) and bright field (BF) STEM images acquired simultaneously. The location of single Pd atoms is circled in the ADF image and superimposed onto the BF image, which is sensitive to the local carbon microstructure. Adapted after Ref. [14].

This finding may have significant consequences for H_2 uptake. Theoretical models [2] predict that transition metal atoms stabilized by carbon structures with sp^2 hybridization may bind up to two or three H_2 molecules per atom (Kubas complexes) with a binding energy intermediate between physisorption and chemisorption, In particular, it was predicted that Pd atoms would resist sintering better than, e.g. Pt atoms, and would bind two H_2 molecules with a binding energy in the chemisorption range (0.6 eV)

and a third molecule in a weakly physisorbed state [1]. This adsorption model has not been verified experimentally because previous attempts to stabilize transition metal atoms on SWNT and fullerenes were not successful.

The occurrence of molecularly adsorbed H_2 on Pd atoms in Pd-ACF is not yet confirmed in this study. A strong and broad energy loss at ~ 40 eV was found in all INS spectra of Pd-ACF samples and only in presence of H_2. The band is quenched by pumping H_2 out, and its position matches a normal vibration frequency of Pd-$(H_2)_3$ [15]. However, more characterization work is required before this feature is assigned to hydrogen bound by isolated Pd atoms or dissolved in small Pd hydride particles.

Conclusions

Pd-modified activated carbon fibers exhibit Pd particles with sizes covering a broad range - from large nanoparticles (between 5 and 40 nm) to atom clusters and numerous isolated Pd atoms - in close contact with the activated carbon support. It is believed that, because of this wide range of particle sizes, the uptake of hydrogen on Pd-ACF follows several mechanisms. The dominant mechanism is physisorption on the activated carbon support. In addition formation of Pd-hydrides on Pd nanoparticles contributes in part to the measured uptake. The β-$PdH_{0.66}$ phase, destabilized by the carbon support, acts as a source of H atoms that spill over to the microporous support, and either recombine or bond to unsaturated carbon atoms. In a narrow range of pressures and temperatures, the kinetic advantage of the spillover process overlaps with the thermodynamic advantage of physisorption and contributes to enhanced uptake. Isolated Pd atoms, identified by electron microscopy, may also induce molecular chemisorption in Kubas-type complexes, but this mechanism still needs to be confirmed.

Acknowledgments

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