

IV.H.4 Atomistic Mechanisms of Metal-Assisted Hydrogen Storage in Nanostructured Carbons

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Objectives

- Establish scientific bases for designing the “building blocks” of nanoporous carbons and metal-doped carbons that enable synergistic interactions leading to enhanced hydrogen uptake at near-ambient temperatures.
- Identify local atomic structures in disordered carbons and metal-doped carbons, explore the nature of hydrogen binding in such sites and the role of metal particles, and understand the mechanism of hydrogen adsorption and the properties of adsorbed hydrogen.
- Characterize and model medium-range order of carbon in the partially amorphous-partially graphitic structure of nanoporous carbons.
- Understand the mechanism of molecular activation of H₂ by metal catalyst particles and of the transfer of hydrogen across the metal-carbon interface.
- Characterize the energetics and dynamics of hydrogen species confined in pure- and metal-doped carbons.

Abstract

Hydrogen storage by adsorption on materials with high surface area and a wide range of molecular-scale porosity comes close to the some of the DOE target levels, but only at cryogenic temperatures. None of porous adsorbents known today allow reaching satisfactory uptake levels at near ambient temperatures. When adsorption is based on van der Waals interactions only, enhancing the uptake levels for hydrogen at temperatures far from its critical point (33 K) is a great challenge. Key to enhanced adsorption is local structure of the adsorbent. The simple picture is that H₂ molecules need sufficient neighbors to bind them, while also allowing sufficient pore volume for storage and for cyclic charging/

discharging. This picture neglects, however, the details of local atomic arrangements. Optimizing local structures for adsorption is difficult even for ordered carbon materials (nanotube bundles, carbon nanofibers etc), and is a more daunting task for disordered carbon materials.

It was empirically observed that adding metal promoters to porous carbon materials could enhance hydrogen uptake at near-room temperatures beyond the limited capacity of pure carbon supports. At least three mechanisms have been proposed to explain this behavior: (1) multiple covalent binding of H₂ molecules to isolated transition metal atoms stabilized by carbon (the Kubas mechanism); (2) dissociation of H₂ on metal catalyst particles and migration of H atoms on the carbon surface to new storage sites (the spillover mechanism); and (3) enhanced physisorption through polarization of H₂ molecules by discrete charges on metal ions (Li⁺, K⁺ etc). The Kubas mechanism is based on theoretical predictions but has not been verified experimentally because of difficulty of stabilizing single atoms of transition metals on carbons. The spillover mechanism is well established in heterogeneous catalysis, and has been often used to explain enhanced H₂ uptake on metal-doped nanoporous carbons compared with the uptake on metal-free carbons. However, spillover remains elusive and escapes direct proof with analytical methods. The third mechanism received only marginal attention.

In this project we focused on developing realistic models of nanoporous carbons that allow understanding the role of local atomic structure, composition, and order on the mechanisms of H₂ adsorption. The task is challenging because of the lack of clear atomic picture of nanoporous carbon materials. We have addressed this challenge using existing expertise at ORNL, including strengths in materials synthesis, advanced X-ray and neutron scattering techniques for characterization of disordered materials, electron microscopy with sub-Ångstrom resolution, and atomistic modeling of structure, dynamics, and adsorption in carbon nanostructures. Our specific goals include (1) identification of atomic structures in disordered carbons and metal-doped carbons; (2) exploration of the nature of hydrogen binding on such sites and of the role of metal particles and modifiers; (3) identification of H₂ adsorption mechanisms and characterization of energetics and dynamics of adsorbed hydrogen.

Progress Report

We made the experimental observation that H₂ uptake by Pd-modified activated carbon fibers (Pd-ACF) is about 30% higher than on metal-free activated carbon fibers (ACF) even

after subtracting the amount of H_2 needed to convert all Pd to Pd hydride (Figure 1c). Using in situ X-ray diffraction and inelastic neutron spectroscopy, we obtained evidence of two elementary steps of the spillover process: (i) destabilization of saturated Pd-hydride by the carbon support and easier release of H atoms to carbon [1]; and (ii) formation of new C-H bonds by chemisorption of mobile H to unsaturated C atoms [2].

Furthermore, examination of Pd-ACF by high resolution scanning transmission electron microscopy (HR-STEM) confirmed that single Pd atoms are stable in the nanoporous carbon matrix (Figure 1a,b) and their concentration was determined [3]. This fact led us to examine whether the Kubas mechanism is energetically favorable for Pd atoms on graphenes (Figure 1d). First principles calculations showed that, in the pressure and temperature conditions of H_2 adsorption measurements, each Pd atom can bind up to four H_2 molecules. Comparison with the experimental uptake (Figure 1c) showed that, although enhanced Kubas binding is a viable route, it cannot substitute for the spillover mechanism. It follows that the enhanced uptake at 300 K is the result of physisorption on carbon support, Kubas-type binding of H_2 to single Pd atoms, conversion of Pd nanoparticles to Pd hydride, and spillover by release of H from destabilized $PdH_{0.6}$ followed by H diffusion on carbon surface and remote storage by either chemisorption or physisorption [4]. Of all these mechanisms, physisorption to

the nanoporous carbon support remains the most important (and limiting) mechanism; spillover may play a lesser role than what has been previously thought.

Doping nanoporous carbon with alkali metals can also promote enhanced H_2 uptake through the mechanism of polarization-induced physisorption. We found out that a high surface area wood-derived ultramicroporous carbon (UMC) has very high H_2 uptake (0.8 wt% at 300 K and 20 bar) compared with ACF and other activated carbons at the same conditions. This atypical behavior cannot be attributed solely to its particular pore structure. However, this carbon has traces of K and Na (residual from chemical activation) which may explain both the large uptake and the hysteretic behavior based on the concept of polarization-induced physisorption of H_2 on alkali ion sites [5].

To confirm this mechanism, we doped a polymer-derived carbon (PFAC) with 0.2 wt% K and observed enhanced uptake at 298 K compared with the pure carbon. Adding K to PFAC also increased the isosteric heat of adsorption by 35% at low coverage (from 16 to 23 kJ/mol at 0.125 mmol H_2/g) and by 8% at high coverage (from 14 to 15 kJ/mol at 0.5 mmol H_2/g). These values of heat of adsorption measured at near room temperatures are in the range considered optimal for practical adsorptive hydrogen storage. However, the amounts adsorbed are still very low, limited by the small volume of narrow nanopores available for adsorption.

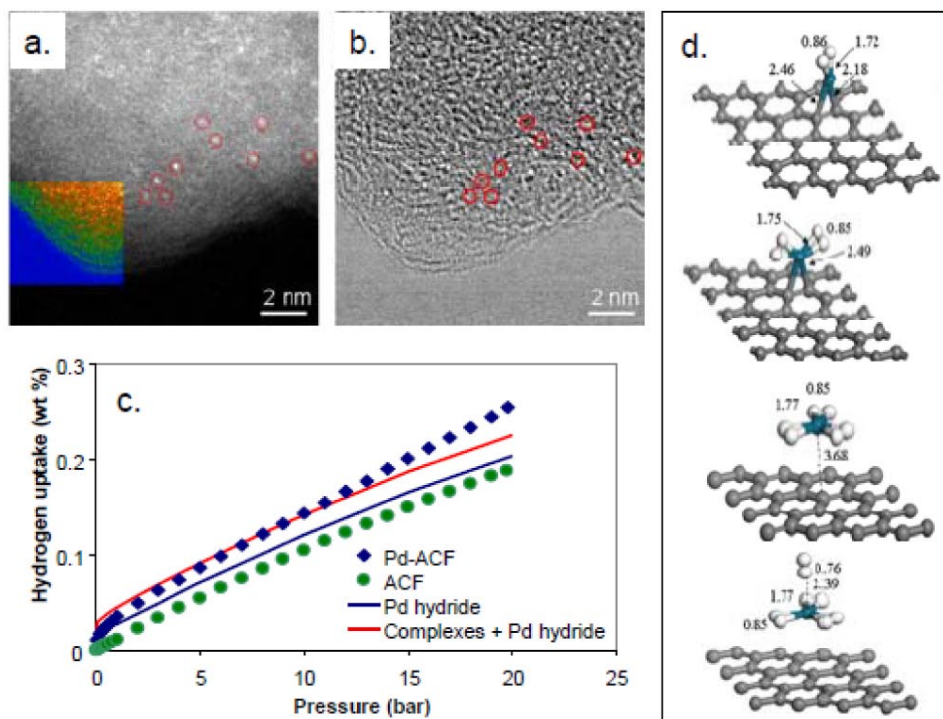


FIGURE 1. (a) Single Pd atoms and (b) carbon structures identified by HR-STEM; (c) experimental H_2 adsorption on ACF and Pd-ACF compared with behavior expected if all Pd is converted to Pd hydride and based on Kubas mechanism hypothesis; and (d) predicted Kubas structures for multiple bonding of H_2 to single Pd atoms.

Adsorption on UMC, although higher than on ACF and PFAC, is remarkably slower, and desorption shows a strong hysteresis. We explored the effect of physically mixing UMC with Pd black (10 wt%) on the amounts adsorbed and the adsorption kinetics. Figure 2a,b shows that the amounts adsorbed on Pd-UMC mixtures (after subtracting the amounts needed to convert Pd into Pd hydride) did not increase significantly at the temperatures studied. However, physically mixing Pd black with UMC has a significantly accelerating effect on the rates of adsorption (Figure 2c) but did not affect the rates of desorption [6]. This behavior indicates again that Pd initiates H spillover to carbon particles with which it is in close contact, and therefore adsorption is faster. However, spillover cannot further increase the (already large) storage capacity of UMC, which is limited by its pore structure, surface area, and concentration of residual alkali ions. Desorption from Pd-UMC mixture is not faster because

hydrogen molecules adsorbed on UMC are not in direct contact with the Pd powder (which is a separate phase) and therefore the inverse spillover process cannot be initiated.

The data presented above suggest that narrow nanopores in carbons are strong adsorption sites for H_2 . Because of the large heat of adsorption (15-20 kJ/mol) these sites should afford high densities of adsorbed hydrogen. Knowledge of the density of hydrogen adsorbed in pores is critical for designing better adsorption systems. However this information has not been reported before, because of numerous experimental complications. We used in situ high-pressure small angle neutron scattering (SANS) experiments at room temperature and an improved high-pressure cell with modified geometry and obtained for the first time direct estimates of the density of H_2 trapped in carbon nanopores (Figure 3a) [7]. The data show clearly that, *at room temperature* and for any given external pressure, the density of confined H_2 is much higher

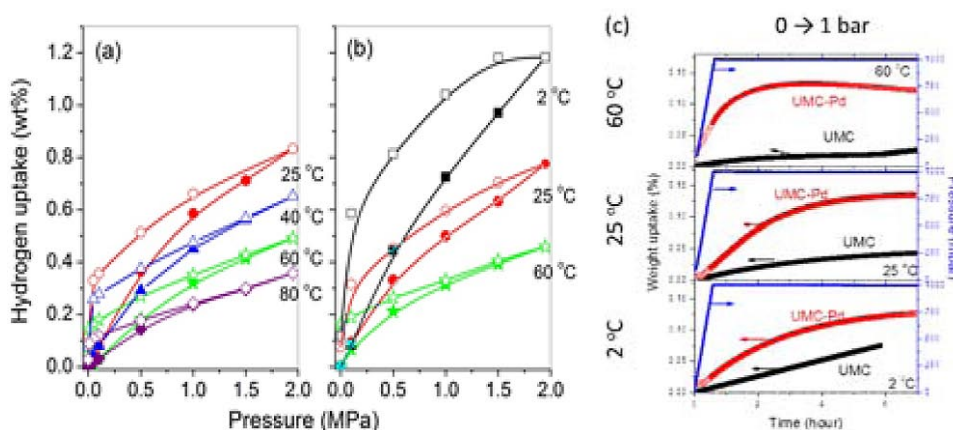


FIGURE 2. Effect of temperature on hydrogen adsorption-desorption isotherms on UMC (a) and Pd-UMC physical mixture with 10 wt% Pd (b) and on the rates of adsorption (c) at equal pressure increments. The additional amount of hydrogen needed to convert all Pd into saturated Pd hydride in physical mixtures has been subtracted.

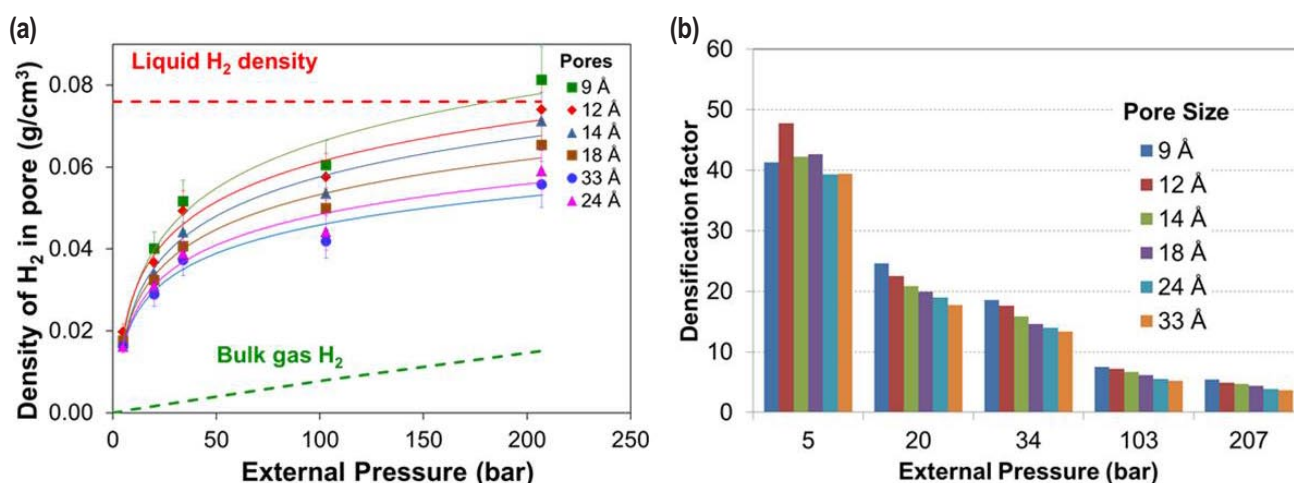


FIGURE 3. (a) Estimated densities of H_2 trapped in PFAC nanopores as a function of pore size and external H_2 pressure, and (b) the densification factors showing the large increase in density at low pressures and the gradually weaker effect at higher pressures.

than that of the bulk H_2 gas and approaches the density of liquid H_2 at the highest pressure (207 bar) in the narrowest pores (9 Å) accessed in our experiment. At low pressures, H_2 confined in the narrowest pores experiences densities some 40-50 times larger than the bulk gas; the densification factor decreases with the increase of pressure (Figure 3b). Furthermore, using the equation of state for H_2 , we calculated the corresponding pressure experienced by the confined fluid. The fluid confined in pores has much larger pressures than the external bulk gas. The adsorption energy calculated from the simple relationship between internal and external pressure, $P_{int} = P_{ext} \exp(-E_{ads}/RT)$, is about -10 kJ/mol in the 9 Å pores saturated at 5 bar external pressure, and probably larger at lower saturation levels. With increase in external pressure, as more H_2 is compressed in pores, adsorption becomes weaker, especially in large pores.

Small angle neutron and X-ray scattering patterns show that the porous carbons investigated have a dominant two-dimensional (2-D) character consistent with sp^2 hybridization on C atoms, but with limited (ACF, PFAC) or extremely weak (UMC) interlayer coherent stacking of graphene sheets perpendicular to their main orientation. More information on the local atomic arrangement was obtained by X-ray and neutron atomic pair distribution function (PDF) methods [8]. They allow for studying both local and medium range structures of disordered materials in real space (Figure 4). It was found that in-plane coherence is limited to about 13-14 Å (8-9 hexagon units) and that graphene sheets are likely to have local folds and cusps that limit the extent of flat areas. Depending on the particular carbon's origin (ACF, UMC) the micro-texture defined by graphene stacking in the perpendicular direction is different, which results in different adsorption characteristics.

Theoretical modeling of hydrogen adsorption in nanoporous carbons provided similar results. We used the method of tight binding molecular dynamics (TBMD)

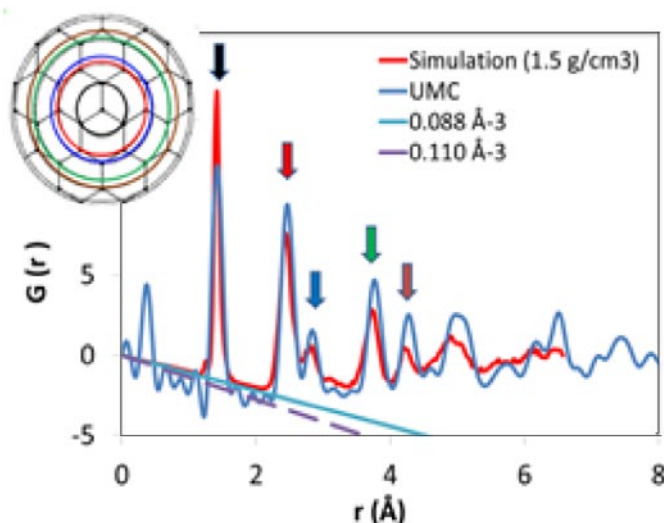


FIGURE 4. Experimental PDF for UMC versus 1.5 g/cm³ simulated structure. The straight line slope scales with atomic density of scattering atoms: 0.088 Å⁻³ (UMC; blue) and 0.11 Å⁻³ (graphite, purple). Insert: origin of PDF peaks graphite structure.

to generate carbon structures with various densities and calculated the amounts of adsorbed H_2 as a function of pressure [9,10]. With increasing carbon density, the structures develop domains of hexagonal symmetry of carbon atoms, interrupted by 5- and 7-atom rings. Hydrogen adsorption calculations identified pockets in the porous structure with favorable adsorption energy (Figure 5a). The heat of adsorption increases with carbon density, but the available volume drops, so that carbon density is an important structural factor that controls practical uptake capacity. These calculations demonstrate that small pores in denser carbon materials adsorb very strongly, with isosteric heat of adsorption at zero coverage limit ranging from 12 to 22 kJ/mol. This range overlaps the range considered suitable

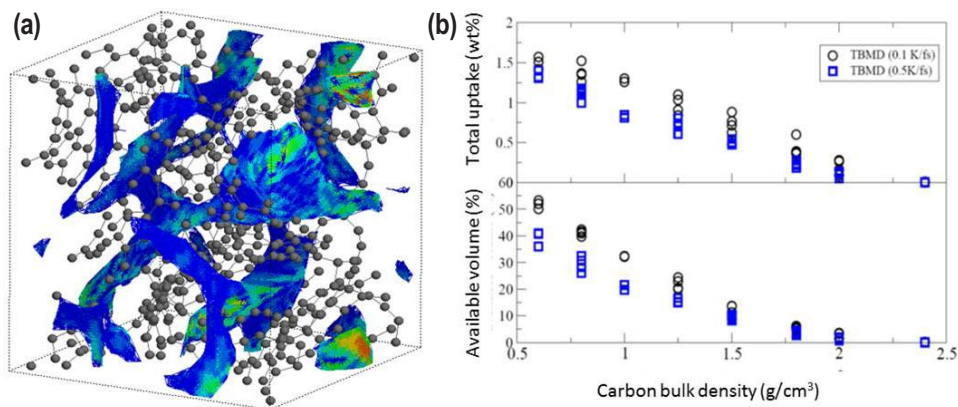


FIGURE 5. (a) Simulated carbon structure (1.25 g/cm³) showing pockets for H_2 adsorption with favorable adsorption energy (< -10 kJ/mol), with blue indicating weaker, and red stronger adsorption sites; (b) Correlation between total H_2 uptake (298 K at 50 bar), available volume, and bulk carbon density. Data show reproducibility between structures obtained in repeated simulations with two quenching rates (black - 0.1 K/fs; blue - 0.5 K/fs).

for hydrogen storage and delivery (15-40 kJ/mol), but the scarcity of these pores that leads to poor uptake. In contrast, although carbons simulated at low densities demonstrate lower heat of adsorption (due to weaker interactions in larger pores), the available pore volume is larger, and the overall effect is an increase in uptake. Figure 5b shows the competition between optimizing the available adsorption volume and optimizing the adsorption potential in narrow pores for high gas uptake.

We emphasize that the results obtained for simulated carbon structures is consistent with the information from in situ SANS experiments which were presented above. The density of adsorbed H₂ in the metal-free carbon is much higher than the bulk-phase density and approaches the density of liquid H₂ even though the ambient temperature is close to 300 K. SANS experiments showed that the density of adsorbed H₂ was larger in narrower pores, in perfect agreement with the image obtained from simulations (e.g. the bottom-right corner of the image in Figure 5a shows high adsorption energy in a narrow pore). Moreover, while the heat of adsorption calculated from SANS experiments (5-10 kJ/mol) corresponds to H₂ adsorbed in high concentrations from compressed gas (5-200 bar), the heat of adsorption obtained from simulations (12-22 kJ/mol) corresponds to strong H₂ – carbon interactions in the limit of zero coverage. The two ranges complement each other, as it is well known that the heat of adsorption decreases with the increase of adsorbed molecules concentration.

Future Directions

Our goal in the few next years is to better understand the relationship between local atomic structure and large scale architecture of nanoporous carbons, and their impact on the nature of interactions with the surrounding gaseous environment, including the phase behavior and properties of molecular species confined in carbon's nanopores.

We will use advanced characterization tools available on the ORNL campus and in other DOE facilities, such as neutron and X-ray scattering, diffraction, spectroscopy; atomic resolution electron microscopy; and powerful computing resources to advance our understanding of fundamental interactions at the atomic and molecular scale between carbon atoms, electronic spins, topological defects, and defectively stacked graphenes; of the interaction with the gaseous environment surrounding nanoporous carbons, of which a large fraction of constituent carbon atoms is exposed at interfaces in porosity. The results acquired during the course of this research will materialize in fundamental understanding of how to design and construct better materials for energy storage and conversion, and the development of new techniques, methods, and procedures that will be transferable to other porous materials of

comparable properties or to other applications operating on corresponding principles.

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