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Properties of immobile hydrogen confined in microporous carbon[☆]

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ABSTRACT

We report results of vibrational neutron spectroscopy investigation aimed to identify the state of hydrogen adsorbed in ultramicroporous carbon. The mobility of hydrogen confined in carbon pores was probed as a function of temperature and pressure using inelastic neutron scattering, and the molecular translational and rotational motions were studied. At low loading rotation of H_2 molecules adsorbed in the smallest carbon pores (~4–5 Å) is severely hindered, suggesting that the interaction between H_2 and the host matrix is anisotropic. At higher loading, H_2 molecules behave as a nearly free rotor, implying lower anisotropic interactions with adsorption sites. At 77 K where bulk H_2 is a gas, deconvolution of elastic/quasielastic signal provide evidence of pressure-dependent fractions of immobile (solid-like) and partially mobile (liquid-like) hydrogen, which correlate with the excess adsorption isotherm at 77 K. Effective H_2 density in pores changes from solid-like to liquid-like with increasing pressure at 77 K. Surprisingly, immobile and partially mobile H_2 is present even at temperatures as high as ~110 K where bulk hydrogen exists only in gas form.

1. Introduction

Hydrogen storage remains the primary bottleneck to be overcome for the successful implementation of hydrogen-based technology in various applications, and is still a major challenge for materials science. In order to find better hydrogen storage materials, different porous materials have been discovered and studied over the years [1–5]. The results showed that the uptake of physisorbed hydrogen is closely connected to the available pore volume and surface area of porous materials. It was found that the presence of micropores (<2 nm), and in particular ultramicropores (<0.7 nm), is most desirable for hydrogen adsorption [6–14], in perfect agreement with theoretical modeling results [15,16]. Carbon materials are among the most investigated adsorbent materials [17] because of their low density, extensive pore structure, chemical stability, low cost, accessibility, and recyclability [18]. Electron microscopy results show that activated carbons consist of isotropic three dimensional networks of wrinkled atomic thin graphene sheets, and that the irregular stacking of crumpled sheets forms micropores of few Å in size [19,20]. The large variation in pore morphology results from differences in raw materials, carbonization, and activation methods [21,22]. Identifying strong adsorption sites and the adsorption mechanism in the microporous activated carbon is necessary to design better host materials for hydrogen storage.

This work presents a neutron vibrational spectroscopy investigation of molecular hydrogen confined in microporous carbon. Vibrational spectroscopy [23] is a well-known analytical technique

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that provides information on structure, bonding, and interactions in chemical systems, with the most popular examples being infrared (FTIR) and Raman spectroscopy techniques. Using neutrons in vibrational spectroscopy studies on hydrogen adsorption takes advantage of the particularly high sensitivity of neutron scattering by hydrogen species. The high penetration of neutrons in solid materials allows studies on adsorbed species and in-pore confined molecular species as well. Moreover, neutron scattering instruments use a variety of sample environments, including in-situ gas adsorption from high vacuum to high pressures, and controlled temperatures from cryogenic to elevated temperatures. Depending on the type of neutron spectrometers it is possible to investigate a multitude of properties in the hydrogen/carbon system. By small-angle neutron scattering (SANS) [24,25] it has been found that the density of H_2 in micropores is about twenty times higher than the bulk gas at ~ 35 bar and room temperature [25]. Higher pressure (~200 bar) results obtained by SANS at room temperature showed that H_2 adsorbed in narrow micropores (<9 Å) reaches the density of liquid hydrogen [24]. These experimental results are in line with empirical estimates according to which H_2 adsorbed in narrow micropores is in a highly dense state [26], most likely liquid [27]. Theoretical predictions for H_2 in narrow slit-shaped carbons led to the same result [28,29]. Challenging the view that the highest densification state of supercritical hydrogen in carbon micropores is the liquid state [9,27], a recent inelastic neutron scattering (INS) study provided direct evidence of solid-like hydrogen immobilized at 77 K at pressures as low as 0.2 bar [30]. Prompted by this result, the main purpose of this work is to further investigate the physical state of H_2 adsorbed in carbon pores using dynamic neutron scattering methods over a broader range of pressures and temperatures. The dynamics of adsorbed H_2 molecules as a function of thermodynamic parameters such as temperature and pressure reveals the nature of the interaction between H_2 and the host matrix, and provides insight into the actual physical state of adsorbed H_2. Recently, quasielastic neutron scattering (QENS) studies on the dynamics of H_2 and D_2 confined in carbon micropores showed that the diffusion onset temperature is higher for H_2 than for D_2 [31]. This observation, which is the opposite to what is predicted by classical physics, is the consequence of quantum behavior at cryogenic temperatures of H_2 and D_2 molecules restricted in the overlapping potential of pore walls in ultramicropores. The QENS study suggests that classical notions of liquid and solid have different signification when applied to H_2 adsorbed in sub-nanometer sized pores [32]. It is important to note that the information on diffusive motion of adsorbed molecules provided by QENS technique is obtained from high resolution measurements (~μeV) of the scattering signal broadening near the elastic peak. It conveys information on both mobile and immobile species. However at higher temperatures it is difficult to determine both components if the instrument is a high resolution QENS spectrometer, since most of the diffusive behaviors will be outside the instrument measurement window. In an inelastic neutron scattering (INS) spectrometer it could be possible to determine the total contribution to the intensity due to both species, although the resolution is oftentimes not good enough to deconvolute the elastic and quasielastic contributions.

The main finding of this paper is the persistence of immobile (solid-like) and partially mobile (liquid-like) H_2 confined in carbon pores over a broad range of pressures and temperatures, including high pressure (up to 40 bar) and supercritical temperatures (up to 110 K). The nature of the interaction potential between H_2 and adsorption sites has been probed by monitoring the para → ortho transition as a function of temperature, pressure, and H_2 loading. In addition, a quasielastic analysis at low energy transfers was performed to the extent afforded by the spectrometer limitations. From the quasielastic signal broadening around the elastic line it was possible to estimate the proportion of immobile (solid-like) and partially mobile (liquid-like) species as a function of surface loading at 77 K. The results showed that the effective density of pore-confined H_2 at 77 K depends strongly on pressure and local pore width. This work demonstrates that the previous observation by one of the co-authors of immobile H_2 above its critical point [30] was not an isolated finding, but a part of a general behavior of in-pores confined H_2. The significance of these findings reaches beyond the immediate interest in adsorption theory and confined fluids behavior, and is expected to infuse a new impetus into the search for the optimal hydrogen storage material.

2. Experimental

Ultramicroporous carbon (UMC) is a chemically activated porous carbon made available by MeadWestvaco Corporation (Charleston, SC) [33]. Gas adsorption characterization of surface properties [22] established that UMC has high surface area ($S_{BET} = 2450\ m^2/g$) and high total pore volume ($V_{tot} = 1.19\ cm^3/g$). The pore size distribution calculated from N_2 and CO_2 adsorption is presented in Fig. S1 of Supporting Information. About 70% of V_{tot} is contained in micropores (<20 Å), and 20% of V_{tot} comes from ultramicropores (<7 Å). Quantitative analysis of SANS patterns recorded for the “dry” UMC material (in vacuum, before exposure to hydrogen) produced similar conclusions [34]. Hydrogen adsorption on UMC shows unusually high uptake capacity at 25 °C (0.8 wt % at 20 bar) with slow kinetics and desorption hysteresis [22,25]. Adsorption of H_2 at 77 K reaches 5.5 wt % at 20 bar, which is comparable with the best known activated carbons (e.g. Maxsorb, AX-21) often referenced as standards for cryogenic H_2 physisorption. The excess adsorption data measured volumetrically (up to 1 bar) and gravimetrically (up to 20 bar) at 77 K are shown in Fig. S2 of Supporting Information. High pressure adsorption data were fitted using the Unilan isotherm, which is an extension of the Langmuir model for patch-like surfaces consisting of energetically uniform patches [35]. Using this model is was possible to extrapolate the adsorption isotherm at 77 K up to the highest pressure (40 bar) of current INS measurements. The Unilan parameters were used to estimate the H_2 loading, q_P, after exposure to various pressures (P) at 77 K. The corresponding relative surface coverage degree, θ_P, was calculated by normalizing to the asymptotic saturated adsorption amount ($q_s = 32.5$ mmol/g) obtained from fitting the Unilan isotherm. Details are available in the Supporting Information file.

Inelastic neutron spectroscopy (INS) measurements were carried out on the VISION spectrometer at the Spallation Neutron Source at Oak Ridge National Laboratory. VISION is a particularly powerful neutron vibrational spectroscopy instrument, very similar to its optical counterparts – FTIR and Raman spectrometers – but with a remarkable sensitivity to hydrogen species in a very flexible sample environments. With a broad energy range extending from −3 up to 1000 meV (or 8065 cm^{-1}) VISION offers good resolution (0.10 meV around the elastic line and 1.2% $\Delta E/E$ above 5 meV) in a range of momentum transfer vector Q (1.3–30 $Å^{-1}$) that corresponds to physical lengths between 0.2 and 4.2 Å [36]. Thus, this instrument is optimized for vibrational studies over broad energy ranges. The closest instrument of the same type is the TOSCA apparatus in UK. VISION measures the time of flight of each neutron for a fixed geometry configuration and integrates the signal within certain values of Q. Thus the Q vector information is integrated within a relatively broad range of values in VISION, and generally it is not required for vibrational spectroscopy. Moreover, the distribution of all resolution components is not strictly Gaussian [36].