

Hydrogen Spillover Effect of Pt-Doped Activated Carbon Studied by Inelastic Neutron Scattering

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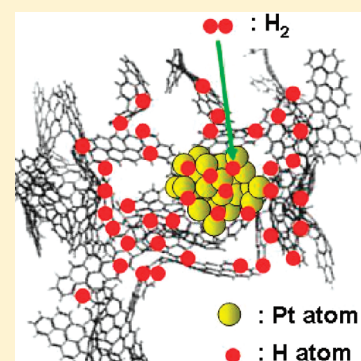
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S Supporting Information

ABSTRACT: We employed the inelastic neutron scattering (INS) method to directly monitor the change of molecular hydrogen in the Pt-doped activated carbon (Pt/AC) samples and provide very conclusive evidence that significant hydrogen atoms can diffuse to the carbon surface at room temperature during the spillover process. The INS method is uniquely capable of revealing the state of the hydrogen (either the atomic or molecular form). The INS result shows a direct quantitative evaluation of the amount of hydrogen adsorbed on AC in an atomic form via spillover. Two Pt/AC samples with different spillover effects were studied herein. The spillover behavior related to dissociation, diffusion, and adsorption of hydrogen in the Pt/AC samples at the temperature cycling from 4 up to 300 K was investigated by this INS study. The present study proposes the concept of diffusion length and hydrogen-rich domain around a Pt cluster center in this system based on INS data.

SECTION: Energy Conversion and Storage



The metal-doped porous material as the prominent hydrogen storage medium via the spillover effect is one of the potential ways to reach the on-board hydrogen storage criteria set by the Department of Energy (DOE), U.S.A.^{1,2} The enhanced hydrogen storage capacity at room temperature (RT) observed by previous experiments due to spillover effects in metal-doped activated carbons (Pt/AC) has attracted large interest worldwide. However, the spillover mechanism in hydrogen storage materials is still very poorly understood,^{2–5} despite decades of studies and applications of the spillover effect in the catalysis field. This poor understanding makes it extremely difficult to reproduce some of the earlier results and has caused a lot of debate.^{6–9} Therefore, the experimental understanding of the spillover mechanisms is crucial for further optimization of materials.

One fundamental assumption of the spillover mechanisms is that hydrogen molecules can be dissociated by the doped metal clusters on the carbon surface, and the resulting hydrogen atoms can diffuse away from the metal clusters and bind to the surface of the porous materials. Despite a plethora of computer simulation results and some qualitative experiments showing the possibility of surface diffusion of hydrogen atoms due to the spillover,^{10–12} there is actually no direct quantitative evaluation of the amount of adsorbed hydrogen in an atomic form, which causes many

debates on the fundamental assumption of spillover effect in hydrogen storage materials. A very recent report¹³ has claimed that a Pt-decorated SWNT (single-walled nanotube) could take a 1.2% mass fraction of hydrogen by forming C–H bonds. However, the conclusion is made by indirect estimation based on ex situ X-ray photoelectron spectroscopy measurements of the Pt-decorated SWNT after H₂ exposure.

In this paper, we have applied the previously proposed inelastic neutron scattering (INS) method (the details of this method will be addressed in a different paper) to directly monitor the change of molecular hydrogen in our sample and provide very conclusive evidence that significant hydrogen atoms can move to the carbon surface at room temperature although the total amount of hydrogen adsorbed in carbons in our experiment is still not very large. Our results provide direct support to the key assumption of hydrogen spillover mechanisms and may thus be useful for material optimization for better hydrogen storage materials utilizing the spillover effect. This method is uniquely capable of revealing the state of the hydrogen (either atomic or molecular forms) and

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its interaction with adsorbent materials. Especially, its capability to monitor the rotation transition of hydrogen molecules provides a way to detect the change of the amount of molecular hydrogen inside of materials.¹²

Two Pt/AC samples with different Pt sizes were synthesized and carefully characterized (Supporting Information). These two samples with the average Pt cluster sizes of 4.2 and 1.6 nm are denoted as Pt/AC_1 and _2, respectively. The Pt concentration was determined using inductively coupled plasma mass spectrometry (ICP-MS) to be 3.32% mass fraction and 0.79% mass fraction in the Pt/AC_1 and Pt/AC_2 samples, respectively. The gravimetric hydrogen storage at RT for the similar Pt/AC_2 sample was measured using an intelligent gravimetric analyzer (IGA)¹⁴ (Figure S1; Supporting Information), and its hydrogen uptake at RT reached 1.0% mass fraction at ~ 66.7 kPa (~ 500 Torr), as shown in Figure S1 (Supporting Information). The undoped AC precursor adsorbed $\sim 0.018\%$ mass fraction of hydrogen at similar pressure and temperature (Figure S1, Supporting Information). The significant improvement of hydrogen storage at such a low pressure indicates that the mechanisms cannot be explained by physisorption alone; thus, it is very tempting to attribute this to the spillover effect (enhancement factor > 50). To confirm our speculation, we need to investigate if there is formation of hydrogen atoms. Because the IGA technique only monitors the mass change of a sample and could not differentiate atomic hydrogen from molecular hydrogen or hydrogen associated with metal, we have performed the INS measurement on both samples using the filter analyzer neutron spectrometer (FANS)^{15,16} at the center for neutron research of the National Institute of Standard and Technology, U.S.A. The INS spectra (energy transfer range: 5–45 meV) were used to identify the molecular rotation levels associated with physically adsorbed hydrogen molecules.

We loaded first about 0.1% mass fraction of hydrogen molecules at 77 K, where diffusion from the Pt catalyst to the carbon, that is, the spillover effect, is not expected to happen. We have chosen to load such a small amount of hydrogen molecules based on the following considerations. First, on the basis of previous experience of loading a large amount of hydrogen molecules using similar methods (unpublished results), the backgrounds are dominated by the signal from molecular hydrogen. It will be difficult to observe a small change of intensity due to spillover effect. Second, as shown in Figure S1 (Supporting Information), the hydrogen adsorption isotherm curve shows a very steep increase at very low pressure, which indicates that if there is a spillover effect happening in our samples, such a low pressure should be sufficient to observe the effect. Therefore, with such a small amount of hydrogen, we may maximize the relative change of INS spectra when hydrogen molecules are lost due to the spillover effect.

The sample cell was then sealed for the duration of the experiment with the fixed amount of total hydrogen. The sample was then cooled down to 4 K to take the INS spectrum, as shown as red triangles in Figure 1 after subtracting the background spectrum that was obtained before loading hydrogen. This INS spectrum was thus due to the scattering of only physisorbed hydrogen molecules. The rotational transition peak at ~ 14.7 meV is a characteristic peak of hydrogen molecules when a hydrogen molecule is converted from *para*-H₂ to *ortho*-H₂ at such a low temperature. When hydrogen molecules become hydrogen atoms, the peak intensity at ~ 14.7 meV will decrease. Therefore, we can monitor the intensity change of this peak to

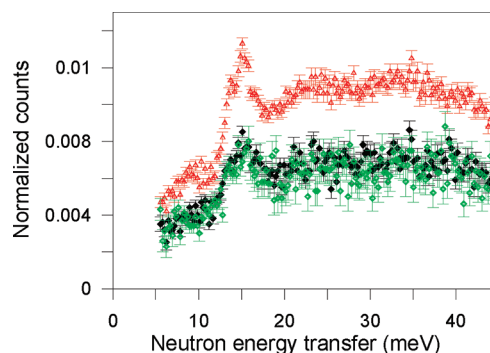


Figure 1. Rotational spectrum of the Pt/AC_1 sample with preloaded hydrogen (red triangle), after the thermal treatment (black circle), and after the second temperature cycling (green diamond). The background spectrum was subtracted from all INS spectra. The sample weight was 1 g. The vertical lines indicate the error bars with one standard deviation.

observe or evaluate the change of the amount of hydrogen molecules in a sample. The broad intensity for energy transfer larger than ~ 14.7 meV is due to the recoiling background of hydrogen molecules.¹² After taking the spectrum at 4 K, we then warmed the sample to RT and kept the temperature at RT for about 6–10 h to allow for the spillover effect. When the sample was warmed to RT from 4 K, the hydrogen molecules physically adsorbed on carbon desorbed and formed a low-pressure hydrogen gas. Then, the uptake by the spillover effect began to occur (i.e., the process of hydrogen molecule dissociation on the Pt particle into the atomic form followed by the migration of spilled-over hydrogen atoms to the material surface). This process may take several hours. The rest of the hydrogen molecules (not converted to the atomic hydrogen by spillover) would be physically adsorbed on carbon upon cooling to 77 K and finally be detected by the rotational transition peak in the INS spectrum. The significant intensity decrease of the peak at ~ 14.7 meV after the thermal treatment is evidence of hydrogen molecules converted to atomic hydrogen followed by subsequent diffusion and adsorption due to the hydrogen spillover at RT. The pressure for a 0.1% mass fraction H₂ gas inside of the cell is estimated to be about $\sim 5 \times 10^5$ Pa (5 bar) at RT. The sample was then cooled to 4 K again. We call this procedure to change the temperature from 4 K to RT to 4 K again one “temperature cycle”. The new INS spectrum is shown as black circles in Figure 1. It is very striking to see the significant intensity decrease of the peak intensity at ~ 14.7 meV after the thermal treatment for hydrogen spillover at RT. This reduction of intensity implies the amount of molecular hydrogen transformed into the atomic hydrogen that is then migrated and finally adsorbed on the Pt/AC adsorbent during the RT hydrogen uptake. In addition to the change of the intensity of the rotational transition peak, the recoiling background has a significant decrease that is almost proportional to the intensity change of the rotational transition peak. If there is only the decrease of the rotational transition peak without the decrease of the recoiling background, the intensity decrease at 14.7 meV could not exclude the possibility that some hydrogen molecules are bound to much stronger sites after a temperature cycle with an extremely large local potential barrier for a quantum rotor, which will cause the peak at 14.7 meV to split into several peaks with significant energy shift so that the peak intensity can have a small decrease. When hydrogen is bound as a hydrogen atom such as a C–H bond, the recoiling background should show

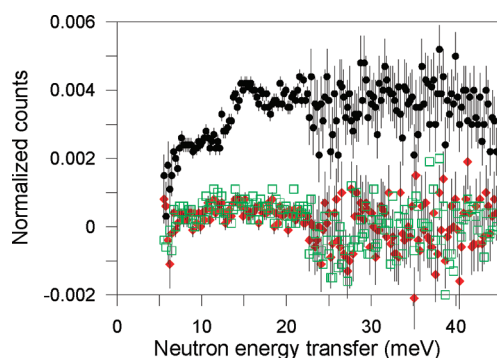


Figure 2. Rotational spectrum of the Pt/AC₂ sample with preloaded hydrogen (black circle), after the first temperature cycling (red triangle), and after the second temperature cycling (empty green square). The sample weight is 0.4 g. The vertical lines indicate the error bars with one standard deviation.

significant loss due to the loss of hydrogen molecules. Therefore, the simultaneous decrease of the rotational transition peak and the recoiling background indicates that the majority of hydrogen atoms do not combine together to form hydrogen molecules again and stay in the atomic state when the temperature is decreased. In order to make sure that the sample cell is not leaking during the experiment, we performed one more temperature cycle without touching the sample cell and obtained the INS spectrum, shown as green diamonds in Figure 1. The intensity is about the same as the intensity after the first temperature cycle, indicating that the intensity loss of the INS spectrum after the first temperature cycle is not due to leakage and that the sample is saturated with hydrogen atoms after the first cycle. There is no increase of total hydrogen atoms due to further temperature cycles.

Assuming that the total amount of hydrogen molecules is proportional to the area of the rotation transition peak at ~ 14.7 meV, we have estimated that about 0.03% mass fraction of hydrogen molecules are converted to hydrogen atoms and remain on the Pt/AC₁ sample after cooling to 4 K. Therefore, using the amount of converted hydrogen atoms in our sample, the H/Pt ratio is estimated to be about 1.8; in the catalysis field, the H/Pt is commonly assumed to be 1:1 or less for surface Pt atoms. Hence, a relatively large amount of the hydrogen atoms are not on Pt clusters and have to exist as some form of hydrogen atom interacting directly with the rest of the porous material.

The same type of INS measurement and thermal treatment with the preloaded hydrogen dose of 0.1% mass fraction was conducted for the Pt/AC₂ sample. The results are shown in Figure 2. Black circles, red diamonds, and green squares are the INS spectra for the sample before any temperature cycle, after the first temperature cycle, and after the second temperature cycle, respectively. Because a smaller amount of sample is used, the pressure in the sample cell at RT is estimated to be about 1.5×10^5 Pa (1.5 bar) if we assume that all hydrogen stays as hydrogen gas. Hence, the real pressure in the cell is smaller as the sample adsorbs hydrogen. The experimental results show qualitatively similar behavior as that observed in the previous INS experiment for Pt/AC₁. However, quantitatively, there is more loss of molecular hydrogen molecules. The estimated H/Pt ratio for converted hydrogen atoms is about 25. This indicates that a large amount of hydrogen atoms have to directly interact with the material surface rather than Pt clusters only. However, at this

stage, we still could not conclude what is the decisive factor affecting the quantitative difference of the experimental results in these two samples, although we have speculated that the size of the Pt cluster and sample pretreatment before the experiments might be the possible reasons⁴ (Supporting Information).

From the two INS experimental results, we provide direct experimental evidence that some hydrogen molecules are converted to hydrogen atoms. Although the total amount of hydrogen adsorbed in the atomic form after reducing the temperature to 4 K is not very high (<0.1 % mass fraction), it is large enough to help us generate a general physical picture that is crucial for the understanding of the spillover effect. A relatively large amount of hydrogen molecules are converted to hydrogen atoms in the second experiment. On the basis of the H/Pt ratio, the converted hydrogen atoms cannot be attributed to interaction with the metal and thus must interact with the carbon support. A forthcoming paper (unpublished results) will explore the interactions between the hydrogen atoms and the carbon support and address whether the interaction is with carbon or functional groups present on the terminal sites of the activated carbon material. It has still been unclear and under investigation how the hydrogen atoms interact with the carbon atoms or functional groups in the reversible spillover process for various carbon materials.¹⁷ We have estimated how far the converted hydrogen atoms can diffuse in the carbon zone centered at a Pt cluster, which we call a hydrogen-rich domain. Because the H/Pt ratio contributed by the full-coverage hydrogen on the Pt nanoparticle can be assumed to be 1 or less according to the literature, the H/Pt ratio contributed by the atomic hydrogen adsorbed in a carbon zone around the Pt particle is about 24 in the second INS experiment. This number implies that spilled-over hydrogen atoms are capable of moving to the far field around the Pt particle and then are adsorbed there to form a hydrogen-rich domain and lead to enhancement of uptake. The hydrogen in the domain could be mainly on the graphene surface in a very narrow zone surrounding the Pt particle. According to the Pt size of 1.6 nm (154 Pt atoms) and the H/Pt ratio of 24, we can roughly estimate the lower limit of the size of this hydrogen-rich domain around the Pt cluster allowing the diffusion and adsorption of the spilled-over 3696 hydrogen atoms. Assuming the activated carbon to be similar to graphite with a density of 2.1 g/cm^3 , each carbon atom occupies a volume of about 9.5 \AA^3 . If the graphite were densely packed around a Pt cluster, then the volume of the hydrogen-rich domain would be about $3.5 \times 10^4 \text{ \AA}^3$ if there is one hydrogen attached to each carbon. (This assumption provides a very conservative estimate of the hydrogen-rich domain as lower hydrogen to carbon ratios would extend the domain.) If we further assume that the domain has a spherical-like shape, then the thickness (radius) of this hydrogen domain is about 20 \AA (2 nm). Now, if we consider the porosity of the activated carbon, then the activated carbon density will be less than that of graphite, and the estimated volume for a hydrogen-rich domain will be about $9.5 \times 10^4 \text{ \AA}^3$ (the measured porosity is 0.8 mL/g, i.e., a pore volume fraction of 0.63, which is typical of activated carbons). This means that the thickness (radius) of the domain is about 2.8 nm. Hence, this conservative estimate implies that a H/Pt ratio of 25 corresponds to, at minimum, a H atom diffusion distance of 2.8 nm away from a Pt cluster. The distance will increase if one incorporates the necessary preferential two-dimensional diffusion along the layered stacked graphene structure of the activated carbon, that is, our 2.8 nm estimate assumes possible three-dimensional

diffusion, which is unlikely in stratified activated carbon. Other calculations of diffusion distance in carbon-based spillover systems range from 150 Å at 298 K¹⁸ to 1000 Å at 473 K to 5 mm at 623 K.¹⁹ The latter case shows evidence for spillover in physically disconnected systems. Many DFT calculations indicate that it is very difficult for hydrogen atoms to diffuse on the carbon surface once a C–H bond is formed. Our INS result shows that the spilled-over hydrogen still can migrate away from Pt clusters. However, our results could not tell how it migrates. Also, our INS measurement through a temperature cycle could not fully exclude the existence of chemisorption (strong C–H bonding).

In conclusion, our INS study provides definite evidence of a significant spillover behavior due to the formation of hydrogen atoms and estimates the amount of hydrogen atoms adsorbed on the carbon support. The spillover mechanism related to dissociation, diffusion, and adsorption of hydrogen in the Pt/AC structure is confirmed by this INS study. The concept of diffusion length and hydrogen-rich domain around a catalytic Pt cluster center in this system is investigated.

■ ASSOCIATED CONTENT

S Supporting Information. Gravimetric hydrogen uptake measurement. The details of the structural characterization of SEM, XRD, and SAXS. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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