

IV.C.1c Hydrogen Storage by Spillover

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- To modify carbon (e.g. by oxidation) to increase spillover storage.
- To develop and optimize our new bridge-building techniques for spillover to enhance hydrogen storage.
- To develop direct metal doping technique on carbons for maximum spillover storage.
- To develop synthesis methods for ultrahigh surface area carbons ($>3,500 \text{ m}^2/\text{g}$).
- To obtain a mechanistic understanding for hydrogen spillover in nanostructured materials for hydrogen storage

Accomplishments

- Demonstrated that adsorbed gas molecules, from gaseous impurities (such as methane) in H_2 , can serve as bridges for spillover thereby increase spillover-storage by $>15 \text{ wt}\%$.
- Showed that oxygen surface functionalities on carbon can increase spillover storage on carbon, by a factor of three.
- A class of catalysts has been found for increasing spillover rates - in both directions.
- Showed that spillover-storage is potentially capable of meeting DOE system targets (at ambient temperature).



Introduction

Nanostructured carbons have tremendous potential for spillover-storage at ambient temperature. An added and important benefit for carbon is that carbon is much more stable than MOFs and other materials. The theoretical limit for spillover-storage on carbon is $>8 \text{ wt}\%$ for a carbon with a Brunauer-Emmett-Teller (BET) surface area of $4,000 \text{ m}^2/\text{g}$.

The issues to be addressed are: to increase the spillover amounts and to increase the rates of spillover.

Approach

We are using the templating approach to develop ultra-high surface area carbons. Using these carbons, we are developing the most effective metal doping techniques for spillover-storage.

To address the issues above, we are developing the most effective metal-doping technique as well bridging techniques in order to maximize spillover-storage. To further increase spillover storage on carbons, we

Objectives

- This project is/was working towards the former 2010 system targets including capacity targets of 6 percent hydrogen by weight and 45 grams hydrogen per liter.
- To develop new sorbents to achieve the DOE targets by using nanostructured carbons or other sorbents such as metal organic frameworks (MOFs) aided by hydrogen spillover.
- To develop a mechanistic understanding for hydrogen spillover that leads to hydrogen storage.

Technical Barriers

- General barriers: gravimetric and volumetric storage capacities.
- Rates: uptake rate only (discharge rate exceeds DOE target).
- Lack of understanding for hydrogen spillover.

Technical Targets

To develop hydrogen storage materials to achieve the DOE 2010 targets (see above) at room temperature:

- To develop new bridging techniques to maximize spillover storage.
- To increase the rates of spillover.

are modifying carbon, such as by introducing oxygen functionalities, to increase spillover. We are also developing catalysts to increase the rates of spillover.

Results

In this report, we show the significant increase in spillover by adsorbing an impurity that is commonly found in H_2 such as CH_4 . Clearly, the adsorbed CH_4 molecules serve as bridges for hydrogen spillover. The results also illustrate the significant errors in using the Benson-Boudart method (for estimating the metal dispersion of supported metals) when spillover occurs, particularly that enhanced by gas impurities. All of the adsorbents used in this work were prepared by impregnating a support with chloroplatinic acid (H_2PtCl_6) (Aldrich, 99.9%).

Pt/AX-21: A 6.0 wt% Pt/AX-21 sample was prepared by impregnating H_2PtCl_6 on AX-21 superactivated carbon. The detailed preparation and pretreatment procedures are given in Ref. 4. The BET surface of the AX-21 was $2,880\text{ m}^2/\text{g}$ and that of the Pt/AX-21 was $2,521\text{ m}^2/\text{g}$.

In order to investigate the effect of methane molecules on the spillover of hydrogen from the Pt surface to the AX-21 carbon surface, CH_4 was presorbed at predetermined pressures before H_2 isotherms were measured, as described in the foregoing. The results are shown in Figure 1 and Table 1. Figure 1 shows the effect of CH_4 on hydrogen adsorption. The adsorption capacity of H_2 on Pt/AX-21 varied with the initial pressure of CH_4 . Pre-sorbing with CH_4 in the range of 5.0×10^{-4} to 3.4×10^{-3} atm resulted in significantly increased adsorption of H_2 . From Figure 1 and Table 1, it is seen that the spillover-adsorption amount of H_2 reached the highest value when the initial pressure of CH_4 was at 1.2×10^{-3} atm. At 1.2×10^{-3} atm of CH_4 , the equilibrium adsorption amount of H_2 at 1 atm increased to $8.81\text{ cm}^3/\text{g}$ standard temperature and pressure (STP) from $4.78\text{ cm}^3/\text{g}$ STP without CH_4 , i.e., nearly doubled.

For H_2 storage, high-pressure isotherms were also measured, and the results are shown in Figure 2.

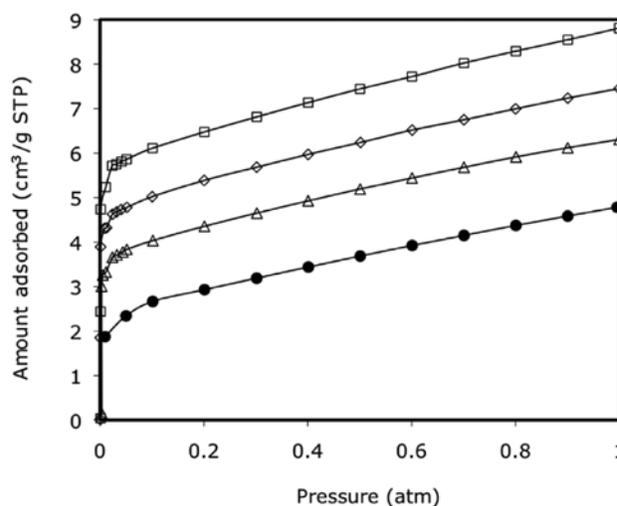


FIGURE 1. Adsorption isotherm of H_2 on Pt/AX-21 at 298 K with presorbed CH_4 at $P(CH_4) = 0$ (●), 5.0×10^{-4} (◇), 1.2×10^{-3} (□) and 3.4×10^{-3} atm (△). The three presorbed CH_4 points fall essentially on the origin due to the large Y-axis scale.

Figure 2 shows that the capacity of pure hydrogen on Pt/AX-21 was 1.20 wt% at 25°C and 100 atm, which was the same with our previous work. The effect of CH_4 on the H_2 storage at high pressures was similar to that at <1 atm. The highest H_2 storage on Pt/AX-21 appeared at 5.0×10^{-3} atm of the initial CH_4 pressure. When the pressure of CH_4 was at 5.0×10^{-3} atm, the H_2 storage reached 1.38 wt%, which was $\sim 15\%$ higher than that of pure H_2 adsorption.

One of the factors determining the spillover-storage amounts is the surface chemistry of the receptor. For carbon, doping by heteroatoms including oxygen may have strong effects. Introducing surface oxygen groups may also have effects. The heteroatom in doped carbon increased the interactions between the receptor and hydrogen, and thus led to enhanced hydrogen adsorption. One may expect therefore, a receptor exhibiting stronger interaction with hydrogen molecules or atoms would be favorable for hydrogen adsorption. In a hydrogen spillover system, the presence

TABLE 1. Results of CH_4 and H_2 adsorption on Pt/AX-21

Initial pressure of PCH_4 (atm)	Saturation Amount of CH_4 (cm^3/g , STP) ^a	Saturation Amount of H_2 (cm^3/g , STP) ^b	Chemisorption Amount of H_2 (cm^3/g , STP) ^c	Platinum Dispersion ^d (%)
0	-	4.78	2.52	73
5.0×10^{-4}	1.5×10^{-2}	7.45	4.92	143
1.2×10^{-3}	3.7×10^{-2}	8.81	5.93	173
3.4×10^{-3}	15×10^{-2}	6.03	3.92	114

^a the saturation amount of CH_4 was obtained at the corresponding initial pressure of CH_4 .

^b the saturation amount of H_2 was obtained at 1.0 atm of H_2 .

^c the chemisorption amounts of H_2 adsorption was obtained at the equilibrium pressure of H_2 extrapolated to zero.

^d dispersion: percentage exposed atoms.

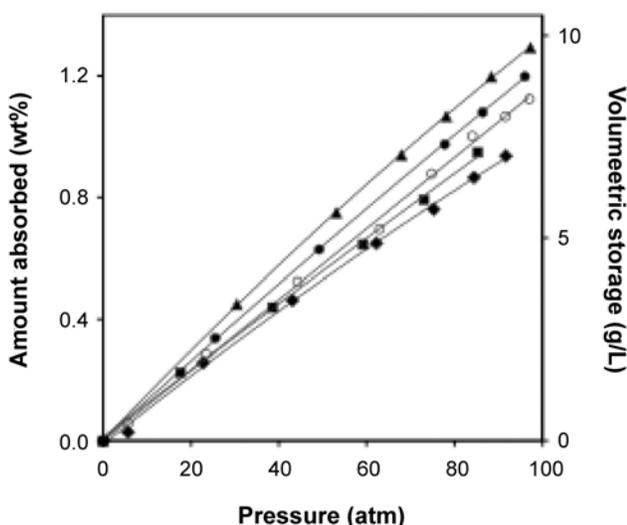


FIGURE 2. Adsorption isotherm of H_2 on Pt/AX-21 at 298 K with presorbed CH_4 at $P(CH_4) = 0$ (\circ), 1.0×10^{-3} (\bullet), 5.0×10^{-3} (\blacktriangle), 1.0×10^{-2} (\blacksquare), and 0.1 atm (\blacklozenge).

of oxygen groups (as will be shown in our molecular orbital calculations) leads to stronger adsorption for the spillover hydrogen, thus an enhanced storage capacity could be expected on an oxygen modified carbon receptor. Compared with boron or nitrogen doping, addition of surface oxygen groups to a carbon receptor is an easy process. As for direct synthesis, graphite oxide is a well-known carbon material with abundant oxygen groups. By considering these aspects, we prepared two different carbons of super-activated carbon (AX-21) and graphite oxide doped with Pd metals, and investigated the effects of surface oxygen in these carbons on hydrogen storage via spillover.

The following three doped carbons were first prepared (using $NaBH_4$ as the reducing agent): 10 wt% Pd doped on AX-21 (Pd/AX-21), 10 wt% Pd doped on oxygen-modified AX-21 (Pd/AX-21-O), and 10 wt% Pd doped on graphite oxide (Pd/graphite oxide). Elemental analysis by X-ray photon spectroscopy ($O/(C+O)$: w/w) indicated oxygen content in Pd/AX-21-O was about 13 wt%, while that in the graphite oxide was approximately 40 wt%. High-pressure hydrogen isotherms at 298 K for plain AX-21, Pd/AX-21 and Pd/AX-21-O samples are shown in Figure 3. In Figure 3, AX-21 exhibited a hydrogen storage capacity of 0.61 wt% at 298 K and 10 MPa, which is in agreement with previous results. By doping 10 wt% Pd on AX-21 sample, the hydrogen uptakes on Pd/AX-21 and Pd/AX-21-O at 10 MPa were enhanced to 0.98 and 1.15 wt%, respectively. It can be seen that both Pd/AX-21 and Pd/AX-21-O samples exhibited much higher hydrogen adsorption capacities than the plain AX-21 sample. The enhanced hydrogen storage capacity cannot be attributed to the differences in surface area because the doped samples have, in fact, lower surface

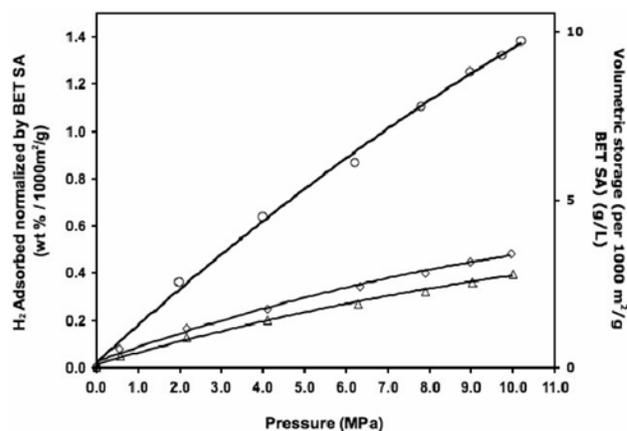


FIGURE 3. High-pressure hydrogen isotherms at 298 K for 10% Pd/graphite oxide (\circ), 10%Pd/AX-21-O (\diamond) and 10% Pd/AX-21 (\triangle), normalized by BET surface area. The BET surface areas are: 2,466 m^2/g for Pd/AX-21 and 2,362 m^2/g for Pd/AX-21-O, and 687 m^2/g for Pd/graphite oxide.

areas than plain AX-21, as is evident from nitrogen adsorption results. The enhancement in hydrogen storage was due to the spillover of atomic hydrogen from metal particles to AX-21. The enhanced hydrogen storage by metal-doped on carbon materials have been observed. It is significant that Pd/AX-21-O had a higher storage capacity than Pd/AX-21. Normalized by the BET surface area, the Pd/AX-21-O adsorbed 22% more hydrogen than Pd/AX-21.

In order to increase the rates of spillover, we explored the doping of metal salts to study possible catalytic effects of Ti and V chlorides on hydrogen spillover on Pt-doped carbon. By doping 2 wt% $TiCl_3$ or VCl_3 , the rates for both adsorption and desorption were significantly increased. The H_2 isotherms on the Pt/AX-21 and metal salt doped samples were similar. The rates were expressed in terms of fractional completion vs. time upon each pressure increase step. The results are shown in Figure 4.

Conclusions and Future Directions

Conclusions

- Adsorbed gas molecules, from gaseous impurities (such as methane) in H_2 , can serve as bridges for spillover thereby increase spillover-storage.
- Oxygen surface functionalities on carbon can increase spillover storage on carbon due to higher heats of adsorption.
- A class of catalysts has been found for spillover rates - for both charge and discharge rates.
- Spillover-storage is potentially capable of meeting DOE system targets (at ambient temperature).

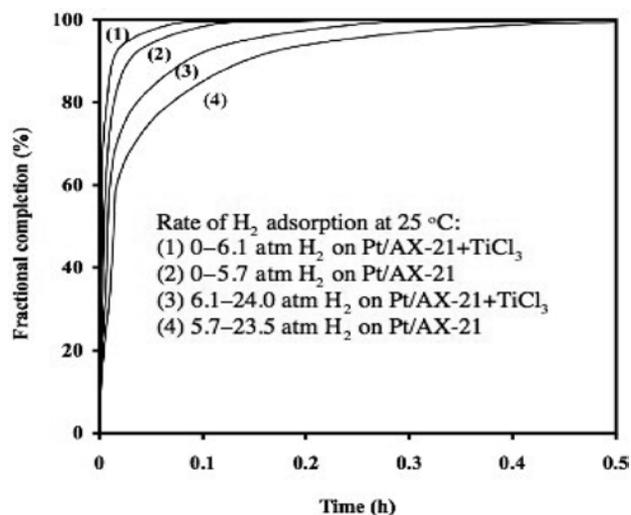


FIGURE 4. Rates of adsorption on Pt/AX-21 and Pt/AX-21+TiCl₃ at 25°C and different pressures. Pressure step: (1) 0–6.1 atm H₂ on Pt/AX-21+TiCl₃, (2) 0–5.7 atm H₂ on Pt/AX-21, (3) 6.1–24.0 atm H₂ on Pt/AX-21+TiCl₃ and (4) 5.7–23.5 atm H₂ on Pt/AX-21.

Future Directions

- Develop oxidized carbons for storage by spillover, particularly on graphite oxides with BET surface areas >1,000 m²/g.
 - Develop sorbents for storage by spillover with bridge-building on MOFs.
 - Obtain a quantitative understanding of kinetics of spillover-storage.
- Develop catalysts for increasing spillover rates for both charge and discharge, and an understanding of catalytic mechanism.
 - Develop new direct metal-doping techniques (including plasma treatments) on AX-21 and other ultra-high-surface-area carbons (i.e., templated carbons) with BET surface areas >4,000 m²/g.
 - Obtain a basic understanding of the spillover process including equilibrium and kinetics, using deuterium isotope.

FY 2009 Publications/References

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