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CODEPOSITION OF THE DEB-PALLADIUM HYDROGEN GETTER SYSTEM

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Hydrogen getters have been used in U.S. Department of Energy components for over 20 years. Current getter systems use an acetylenic organic material with a carbon-supported metal catalyst (1,4-bis [phenylethynyl] benzene [DEB] and palladium/carbon). Traditional preparation of this getter is done by mixing the DEB with palladium and carbon in a ball mill process followed by pressing, remilling, and pelletizing before final assembly into perforated getter support tubes. The tubes are placed in the components in a location somewhat remote from potential sources of hydrogen.

A new chemical vapor deposition (CVD) and physical vapor deposition (PVD) codeposition process has been developed for fabricating the palladium-catalyzed DEB getter. The process involves the codeposition of the DEB/Pd/carbon onto planar and complex surfaces and infiltration into porous substrates using modern CVD and PVD techniques. DEB was sublimed from solid DEB. Palladium and carbon were produced through the UV photolysis (254 nm) of allylcyclopentadienylpalladium, which was synthesized for this project. The DEB and the palladium/carbon precursor are admitted simultaneously to the reaction chamber via bubbler reservoirs. The codeposition processing is simple, low-temperature, scalable, and lends itself well to placing the getter onto complex shapes and substrates of various compositions. The new getter deposition technique offers the potential advantages of high surface area, ease of component surveillance and remanufacture, and intimate contact with source materials evolving hydrogen and those most sensitive to attack by hydrogen. Hydrogen uptake on getter produced by the new codeposition technique has been demonstrated.

INTRODUCTION

The traditional hydrogen getter developed over 20 years ago is a carbon-supported, palladium catalyzed organic (1,4-bis [phenylethynyl] benzene) (DEB) that has been successful but its use has been limited by the size and geometry of the support tubes or other support regimes required in most applications and the major restriction that the tubes present: the getter cannot be brought into intimate contact with the sources producing hydrogen or the materials most sensitive to hydrogen degradation. In the traditional technology 1,4-bis (phenylethynyl) benzene (DEB) is ball-milled with palladium and carbon, pressed to near theoretical density, ball-milled again, repressed in pellet form to a density with the required porosity, then loaded into perforated support tubes.

The major objective of this project was to develop a new, simplified deposition technique that allows the DEB/Pd getter to be deposited over large surface areas, onto complex shapes, and infiltrated into porous structures. Because the DEB/Pd getter has been used and extensively characterized over 20 years and is certified for use in specific components, we were limited to searching for only a new deposition technique and did not have the option of looking at new chemical systems that may have been easier to deposit. Another limitation for any new deposition process is that it could not impart any significant change to the thickness and mechanical properties of the substrate materials. The practical results of the new deposition technique are 1.) to permit the getter mass and surface area to be easily increased in specific components where the limited size does not permit installation of additional getter support hardware, 2.) allow the getter to be placed in intimate contact with materials evolving hydrogen or sensitive to hydrogen exposure, and 3.) simplify surveillance and remanufacture of the components.

Figure 1 shows the DEB/Pd/C hydrogen reaction mechanism. Each molecule of getter has 8 unsaturated carbon bonds. Once reacted with hydrogen, the gettering is not reversible. The specific role of carbon in the gettering process is not clearly understood. It is required for gettering to occur and is assumed to facilitate the movement of the palladium catalyzed hydrogen to the unsaturated carbon sites on the DEB molecule.

EXPERIMENTAL APPROACH

This project uniquely combines chemical vapor deposition (CVD) and physical vapor deposition (PVD) techniques. It was necessary to individually demonstrate numerous technical accomplishments and then integrate these accomplishments into the final codeposition of DEB and Pd/C. It was recognized from the beginning that if any one of the technical goals could not be achieved, deposition of the DEB/Pd/C getter might not be possible from the chosen technique and chemistry.

The codeposition system is a research scale CVD/PVD reaction chamber 10 cm diameter and 25 cm high. The precursors for the codeposition are 1,4-bis (phenylethynyl) benzene and allylcyclopentadienylpalladium (allyl-Pd-Cp). Both precursors are solid at standard temperature and pressure (STP) and are contained within separate heated bubbler reservoirs that are swept with Ar before delivery to the reaction chamber. Figure 2 shows the codeposition system and reaction chamber. The DEB is deposited by sublimation with recondensation on the substrate of choice mounted within the chamber. As the allyl-Pd-Cp enters the chamber, it is illuminated with UV light (254 nm) which dissociates the compound by photolysis yielding palladium and a small amount of carbon. When the DEB and allyl-Pd-Cp are introduced simultaneously, a homogeneous codeposit of DEB and Pd/C results at ambient temperature and 10 Torr. Figure 3 shows the morphology of the codeposit, which is a platelet structure of high surface area considered advantageous for gas-solid interactions.

Basis for use of allylcyclopentadienylpalladium as a palladium precursor is an IBM publication in which a polymer surface was metallized with palladium for subsequent copper plating.[1] This publication showed a known synthesis (McClellan, et. al., 1961) with good stability and efficiency, the volatility required for transport (20 mTorr at 25°C), and the expectation that photolysis by UV would yield a deposit of palladium particles 1000Å diameter.

Synthesis of and manipulations on the allyl-Pd-Cp were done using standard Schlenk line techniques within a Vacuum Atmosphers dry box with a Mo-40-2 dri-train under a helium atmosphere. One equivalent of dimeric allylpalladium chloride in anhydrous benzene was stirred under argon as two equivalents of cyclopentadienyllithium in anhydrous benzene were added. An exothermic reaction occurred immediately, and the reaction mixture turned deep red. After stirring for 60 minutes at 25°C, the reaction mixture was heated to 45-50°C for 30 minutes. After cooling to 5°C, 50 ml of deoxygenated water was added, and the benzene layer separated and dried with anhydrous calcium sulfate overnight. The benzene was removed by distillation and the deep-red, semi-solid residue was sublimed at 45-50°C (10 mm) to give a yield of 84% of allylcyclopentadienylpalladium as deep-red needles. Melting point is 60-62°C.

RESULTS

The DEB/Pd/C hydrogen getter was successfully deposited using the CVD and PVD codeposition technique. Leading to this success required the following steps. Sublimation and recondensation of the DEB without change in chemical structure was demonstrated first. The allyl-Pd-Cp precursor was then synthesized and UV photolyzed to produce palladium particles averaging 0.5 µm diameter which is ideal for incorporation into the getter. The morphology of the particles indicates they are produced by gas-phase nucleation. DEB and Pd/C were simultaneously deposited as a homogenous layer to form the codeposited hydrogen getter. Infiltration into porous substrates has been demonstrated. Since DEB is deposited along with the palladium in an UV environment, the stability of DEB under UV radiation was evaluated and it was determined there is no influence. The long-term stability of the synthesized allyl-Pd-Cp compound was also evaluated and found to be stable in the bubbler under ambient conditions for at least two months. Using H^1 NMR, it was demonstrated the CVD and PVD codeposited DEB/Pd/C material is a hydrogen getter. Figure 4 shows the NMR spectra of unsaturated and fully saturated samples of conventional and CVD and PVD codeposited DEB/Pd/C getter are identical.

CONCLUSIONS

A new CVD and PVD process has been developed for depositing the DEB/Pd/C hydrogen getter. This process affords a relatively simple, cost-effective means of placing the getter over a larger surface area, onto substrates of complex geometry, and in more intimate contact with sources producing hydrogen and components adversely affected by hydrogen attack. Advantages of the CVD and PVD codeposition process are: it is a gas/vapor phase process which is ideal for coating large surface areas and for infiltration of porous structures and it is scalable to large components; it is not geometry limited – complex shapes are possible; it is a room temperature process and substrate friendly; the getter can be doped with other materials and the loading/ratio of the constituents can be varied to customize getter performance; the deposition process is fast, cost-effective, and uses commercially available CVD and PVD equipment; the process is reproducible; the morphology of the codeposit is a fine, platelet structure with a high surface area which is advantageous for gas-solid interactions; the process is one-step and eliminates many processing steps needed for the conventionally processed getter; the codeposit may be coated directly onto surfaces and does not require any support hardware.

There a high level of interest in gettering materials for a variety of industrial applications, including electronic materials, emitters, detectors, sensors, satellite technology, and high explosives. This new process will give industry greater flexibility by placing the getter into applications not possible now with the current conventional getter material or improving existing applications. It may be used in virtually any application where it is desirable to capture and hold hydrogen.

REFERENCES

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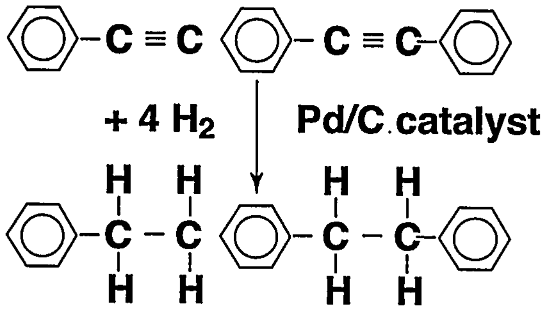
(1,4-bis(phenylethynyl) benzene (DEB)



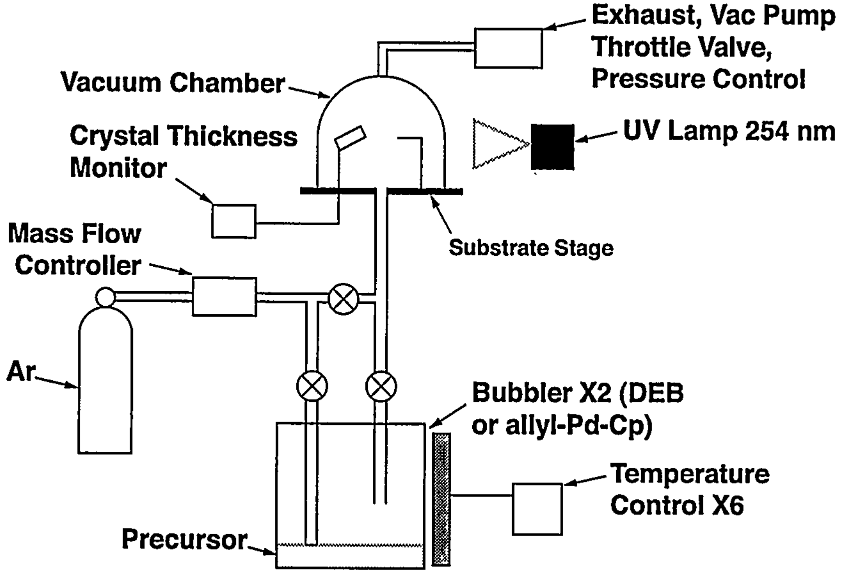
$$\text{Getter} = \text{DEB} + \underbrace{\text{Pd} + \text{C}}_{\text{catalyst}}$$

Melting Point: 179°C
H_2 Capacity: 240 cc-atm/g @ STP
Operating Range: -30° to 80°C
Molecular Weight: 278

from Smith/Schicker

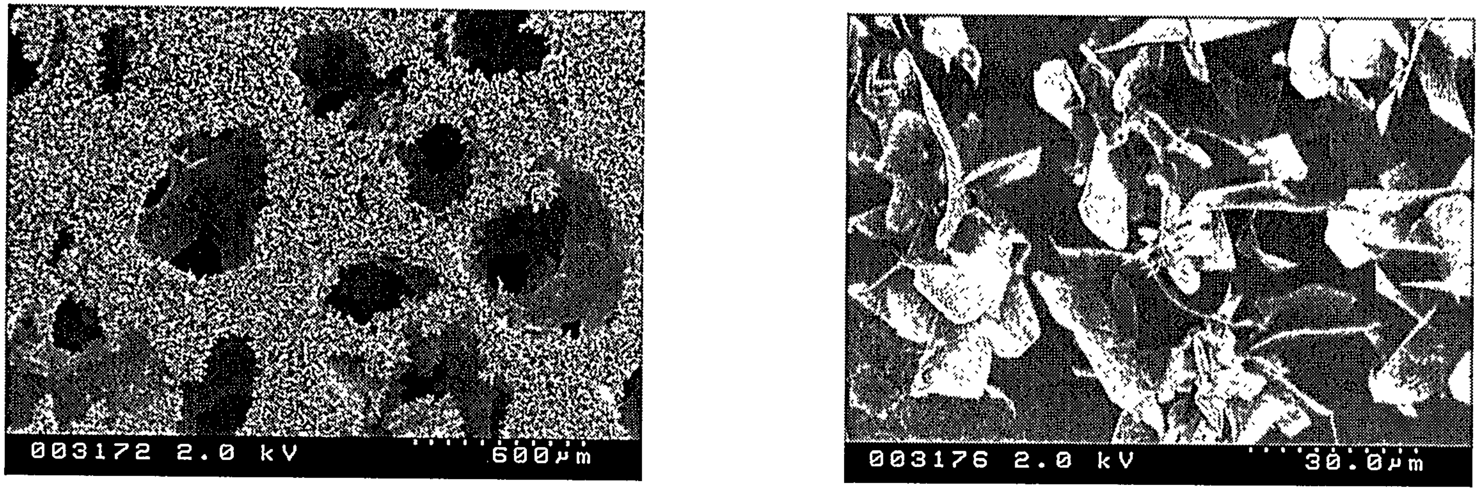
DEB/Palladium Getter Structure-Reaction Mechanism and Physical Data

Fig. 1



Codeposition System Schematic

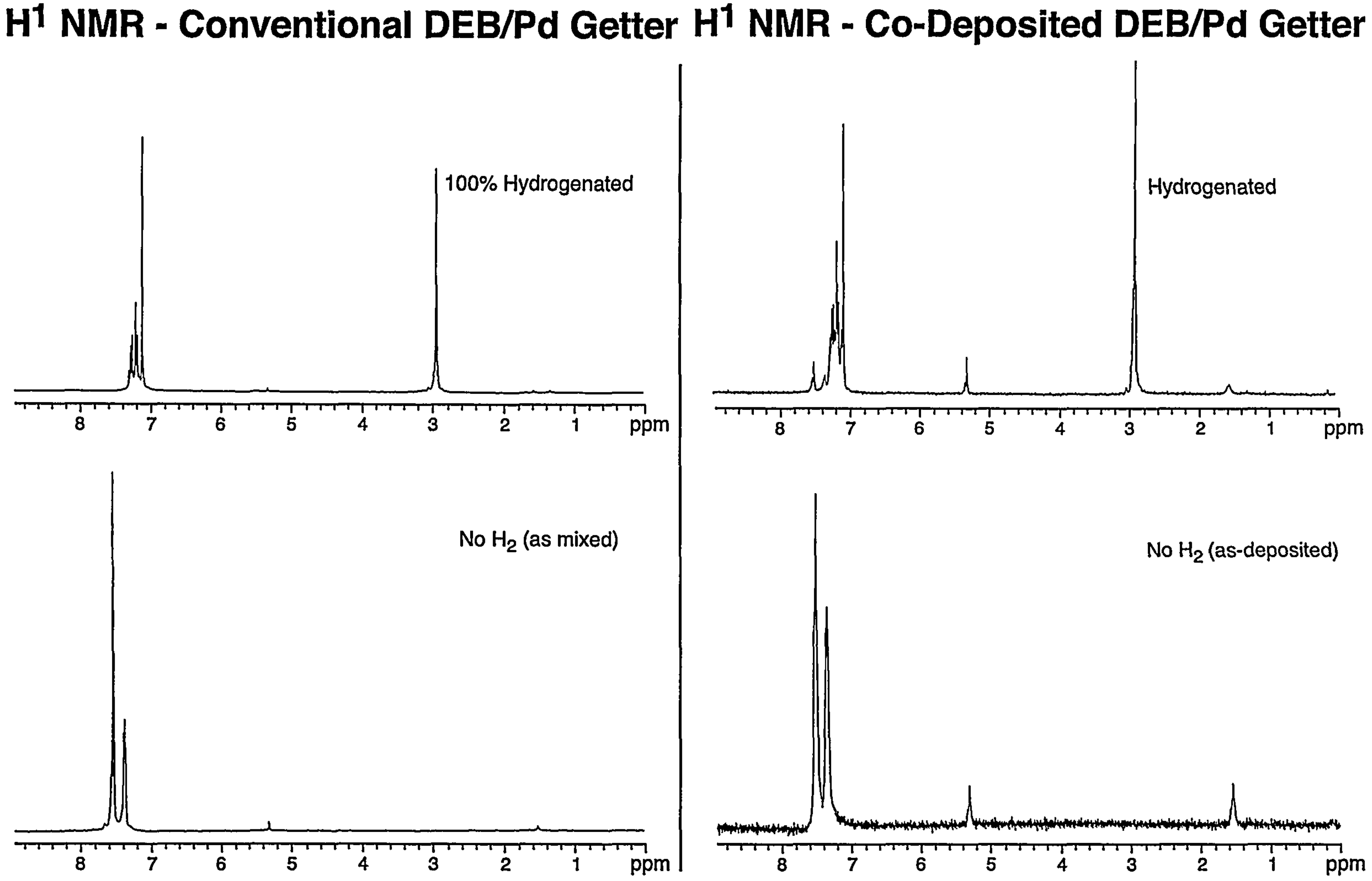
Fig. 2



Palladium and DEB Co-Deposited into Foam

Palladium and DEB were codeposited at ambient temperature. The deposit develops a platelet-like microstructure.

Fig. 3



Appearance of the singlet at 2.9 ppm in the aliphatic region along with the shift downfield of the aromatic region multiplet is indicative of saturation (hydrogenation) of the carbon bonds.

Fig. 4