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Abstract

Herein, we describe hydrogen getter technologies developed at SNL and KCD over the past decade. The technologies are based on the irreversible removal of hydrogen by catalytic hydrogenation of unsaturated organic compounds. Different types have been developed: crystalline getters, dialkynes combined with heterogeneous catalysts; and a polymeric getter, a thermoplastic elastomer capable of reacting with hydrogen in the presence of oxygen without producing water. These materials can remove up to 300 cc (STP) of hydrogen per gram of material, and can maintain atmospheres of less than 10 ppm hydrogen. Crystalline getters for tritium and the combination hydrogen(tritium), water, and oxygen are described.

The accumulation of hydrogen is usually an undesired event. Large leaks from hydrogen storage and handling facilities pose explosion hazards. Small amounts of hydrogen that may build up in sealed containers after long storage times can damage integral components. Any tritium leak is an immediate health hazard. Hydrogen scavengers or getters can avert all of these potential problems by irreversibly removing hydrogen from such environments.

Early hydrogen getters were metals that, though effective, were sensitive to oxygen. More recent work with crystalline organic materials has yielded formulations that will scavenge hydrogen in the presence or absence of air.[1-4] They commonly utilize a catalyst to add hydrogen across a carbon-carbon double or triple bond. A getter that will be stable after reaction with tritium is a further challenge.

In this paper we describe the development of two types of organic getters: the first is a new crystalline getter, based on 1,4-bis(phenylethynyl)benzene[5] (DEB); the second is a polymeric hydrogen getter, based on styrene-butadiene copolymer. Each was

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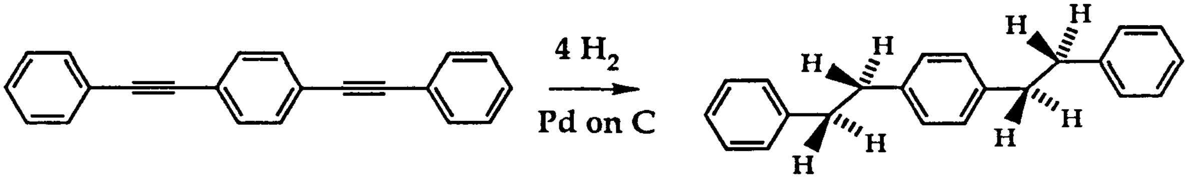
developed with specific properties in mind. They react quickly and completely while containing both fast and slow leaks. The getters work in air or inert atmospheres over a large range of temperature and pressure. Finally the crystalline getters remain stable solids after complete hydrogenation or tritiation so that no material migration occurs.

Crystalline Getters

DEB is a non-toxic, non-mutagenic, crystalline, white solid[5] that when formulated with various catalysts makes an irreversible hydrogen trap. The standard getter formulation has a capacity of 241 cc (STP) hydrogen per gram. Pure DEB melts at 179°C and fully hydrogenated 1,4-bis(phenylethyl)benzene melts at 87°C, so reacted product will remain solid to at least 80°C. The reduction is exothermic and its rate increases with hydrogen pressure. The getter works over a wide temperature range, though the hydrogen uptake rates are slower at low temperatures.

The reduction of DEB getters follow the following stoichiometry:

$$4H_2 + DEB \longrightarrow DEB(H_8)$$



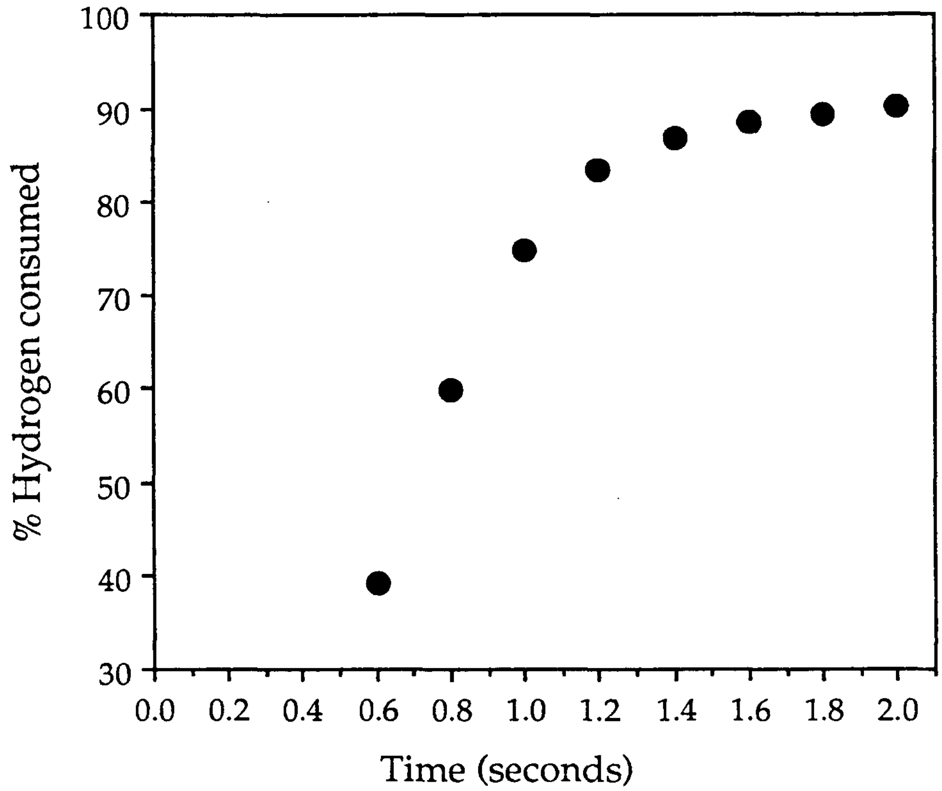
The standard formulation consists of 75% w/w DEB and 25% catalyst (5% Pd on carbon). Other formulations have been used for different applications but this material represents the best balance between reactivity and cost. Where other formulations are used they will be noted.

These materials effectively scavenge hydrogen, deuterium and tritium. They usually react to >90% of their capacity with both high and low concentrations of hydrogen, and have been shown to be stable in the absence of hydrogen up to 18 months (70°C, N_2). Using excess getter at room temperature, residual hydrogen concentrations are reduced to <10 ppm. Other hydrogen getter materials based on DEB have been formulated including: polyethylene composite, urethane adhesive and RTV castable silicone.

Meaningful relative gettering rates at different temperatures are difficult to obtain because the exothermic reaction can alter the chemistry that occurs and the nature of the reactants. Each rate depends both on the physical setup of the apparatus and the distribution of the getter. The table below of initial reaction rates is representative of the increased reaction at higher temperatures.

Temperature	Relative Amounts of Hydrogen Consumed After 25 s
0°C	1.0
23°C	8.6
52°C	14.8

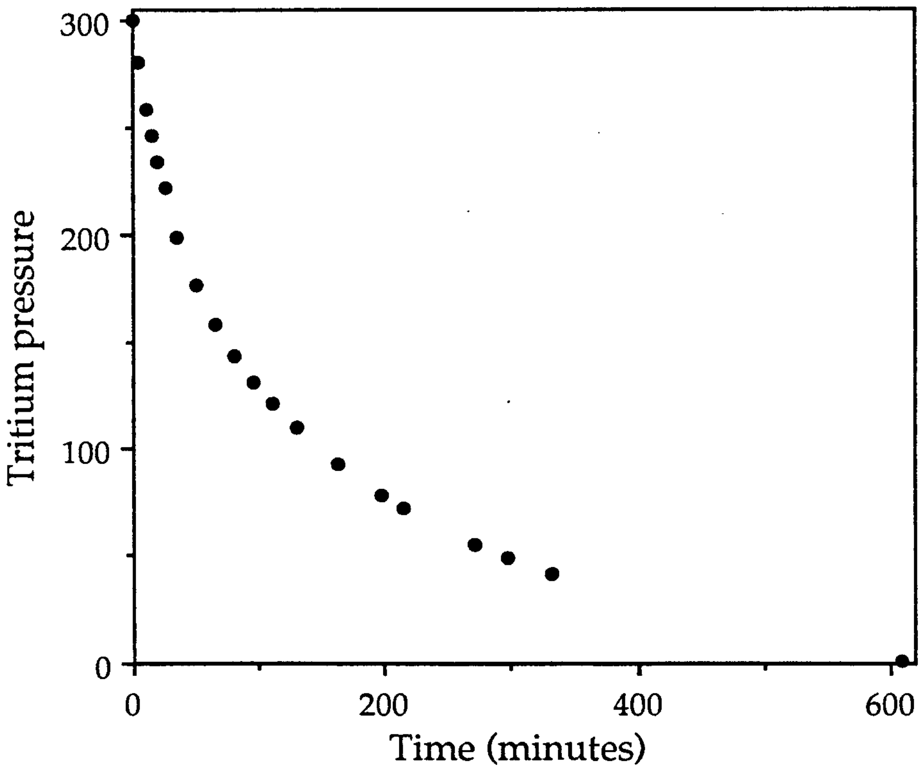
Hydrogen gettering can be an extremely rapid heterogeneous reduction. Under ideal conditions, >90% of the hydrogen can be scavenged in $\approx$ 2 s. These rapid reactions occur only in the absence of other gasses with degassed getter. In most cases, such as in the presence of air, the reaction is slower. A slower reaction is desired for most applications because the exothermic reaction will melt and sinter the getter if allowed to proceed too fast. If rapid uptake is mandatory, large excesses of getter must be used to assure that melting does not occur. As much as 2/3 of the uptake capacity can be lost in rapid reaction scenarios.



Graph 1: This rapid uptake scenario represents the following setup. Hydrogen at 125 psi is expanded 2.3 times into a volume containing ≈ 3.75 times excess of getter (1/1 DEB/10% Pd on C). The expansion equilibration time is 1.16 s, as determined for argon. The graph represents percentage total hydrogen consumed. Measurements were recorded only after the pressure began to drop. The getter is noticeably sintered after this reaction.

To avoid the sintering seen during rapid uptake, another strategy was used: diluting the getter with an inert material, such as in the polyethylene composite mentioned above. Equal portions of standard DEB getter and polyethylene powder, when pressed into a pellet, react with excess hydrogen to >98% of capacity within 100 s. These conditions would cause charring and capacity loss with the plain getter unless large excesses were used. The polyethylene acts as both a heat sink and a diluent, thus slowing hydrogen diffusion and preventing a runaway exotherm.

The standard getter scavenges tritium quickly and completely, then ages safely. A sample loaded to 50% capacity with tritium released only 0.01% of its radioactivity as volatiles after 36 weeks and only 0.06% after 66 weeks. These times are longer than necessary for most shipping container applications. This getter will generate traces of T_2O when scavenging tritium in the presence of air.

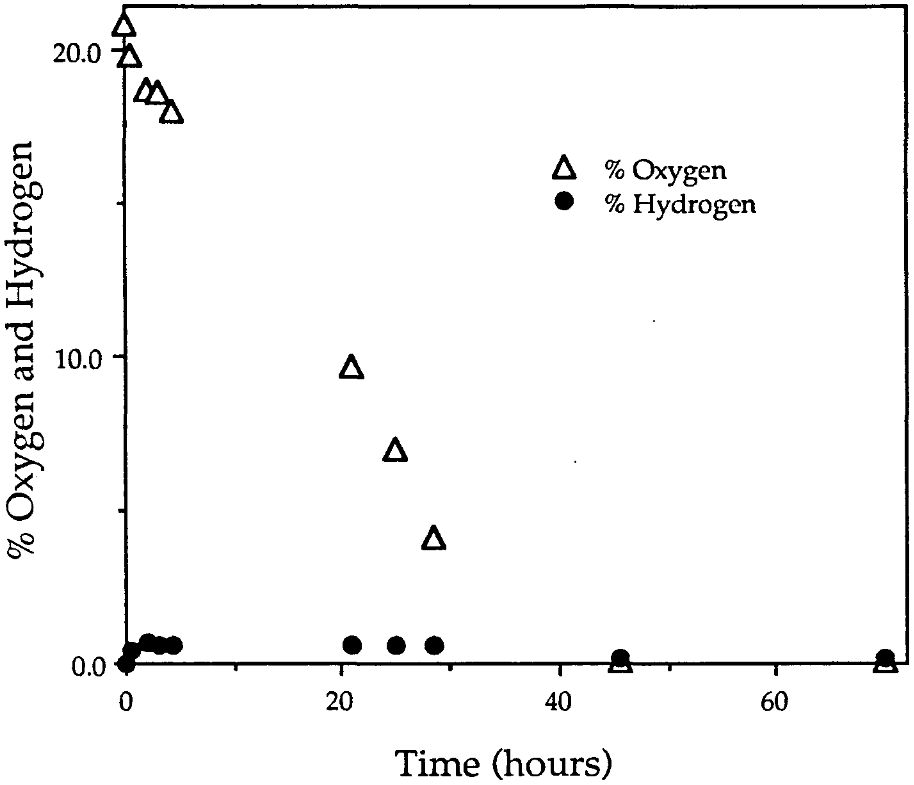


Graph 2: Tritium pressure vs time using the standard getter. Complete uptake represents 50% of the gettering capacity. The overgas was ≈ 3% helium and 97% tritium. After 24 hours, we could not detect a measurable pressure of tritium above the helium background (Sensitivity to <0.1 mmHg).

DEB can also be formulated into a combination hydrogen, water, and oxygen getter especially suited for maintaining a dry, inert atmosphere over long periods in sealed containers. The combination getter contains an additional ≈ 10% lithium hydride (or calcium hydride) that acts to scavenge any water present. Hydrogen generated in the reaction is either combined with oxygen on the palladium catalyst, or gettered by the DEB. The reactions involved are:

1. $H_2O + LiH \longrightarrow LiOH + H_2$
2. $2H_2 + O_2 \longrightarrow 2H_2O$
3. $4H_2 + DEB \longrightarrow DEB(H_8)$

Exact relative rates have not been determined, but in an experiment where an atmosphere of moist air + tritium was exposed to this getter, the radioactivity ended up 69% in the DEB and 31% in the LiOT. This getter, with an adjustable amount of LiH, will scavenge all the $H_2/H_2O/O_2$ from a sealed container and maintain an inert atmosphere. After sealing, the getter removes these common reactive gasses, and as long as its capacity is not exceeded maintains such an atmosphere. This getter is usually used as a powder sealed in fiberglass bags. Residual gas levels are low after complete reaction: Hydrogen <10 ppm, Oxygen <30 ppm, Water <80 ppm. As seen in the graphs below, the rate of the reactions are such that an inert atmosphere is established within 48 hours. The hydrogen concentration shows a transient increase as the water is consumed by the LiH, while the oxygen concentration steadily decreases.



Graph 3: Percentages of H_2 and O_2 vs. time for the desiccant getter. The reaction was performed a sealed, 2 L, air-filled volume spiked with 0.5 g of liquid water, and used 8 g desiccant getter (5 g DEB/Pd on C and 3 g LiH).

The long-term gettering of tritium is more challenging. The β-decay of tritium often destroys organics, breaking them into small volatile pieces that are potentially worse problems than the original T_2 gas. Getters can enhance the safety of tritium-filled devices by acting as secondary confinement. The DEB getters, especially the Pd on C getters withstand high tritium loadings well, releasing only tiny amounts of radioactive volatiles over prolonged aging times. The combination getter is also effective in the presence of tritium though it outgasses more radioactivity than the simple getters. A sample (Pd on Al_2O_3,LiH) loaded at half-capacity of tritium released 0.14% of its radioactivity as volatiles after eight weeks and 0.38% after 33 weeks. We expect a decrease in radioactivity release from the Pd on C combination getter as compared to the Pd on Al_2O_3. This would be the same situation as observed in the tritium-only getters. Though these releases are significant amounts of radioactivity, the absorption of >99% of the tritium yields a much larger safety margin for shipping containers.

The combination getter also solves a problem that plagues tritium getters: that is the generation of tritiated water. The formation of lithium or calcium hydroxide removes the water permanently. The combination getter is formulated with the proper amount of hydride for the amount of oxygen in the sealed container of interest. Contact with bulk acidic materials must be avoided, but trace acidic contaminants simply generate water that is again consumed by the getter.

In practical use the getters have a weakness. In massive, one-time leaks, the getters will react with most of their capacity of tritium rapidly and effectively. In slow leak situations where the getter is called upon to absorb small amounts of tritium over extended periods of time excesses of getter must be used. Partially tritiated getter will lose some of its capacity with time because of radiation damage. Though capacity is lost, the DEB seems to crosslink rather than fragment so radioactive volatiles are minimized. Experiments to determine the time/dose/capacity loss curve are underway.

Polymeric Getters

The polymeric getter, in contrast to the crystalline getter, utilizes a homogeneous hydrogenation catalyst combined with an olefinic polymer.[6] Hydrogenation of polymers in the bulk has been previously demonstrated.[7] The polymeric getter approach simply uses this chemistry to scavenge unwanted hydrogen. The optimized material consists of 1 wt% of the Crabtree[8] catalyst, $[Ir(COD)(Py)(tcyp)]^+PF_6^{-*}$, dissolved in the triblock copolymer polystyrene-polybutadiene-polystyrene (PS-PB-PS). The catalyst is dispersed in the polymer by solvent casting. Electron microscopy (SEM and TEM) analysis suggests that the catalyst is completely dissolved in the polymer matrix. The triblock copolymer is a thermoplastic elastomer containing 72 wt% polybutadiene centerblock. All of the chemistry occurs in the olefinic domains. Hydrogen is consumed as the polybutadiene is converted to a polyethylene-like centerblock.

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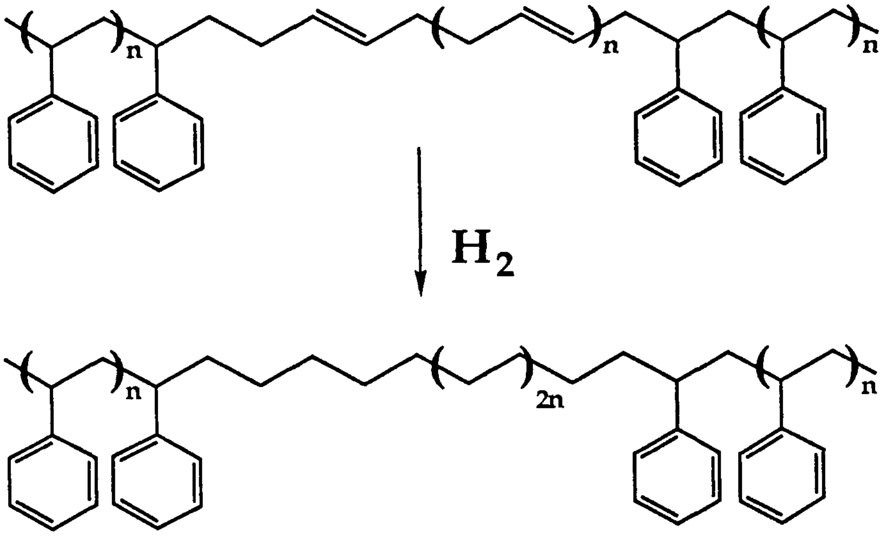
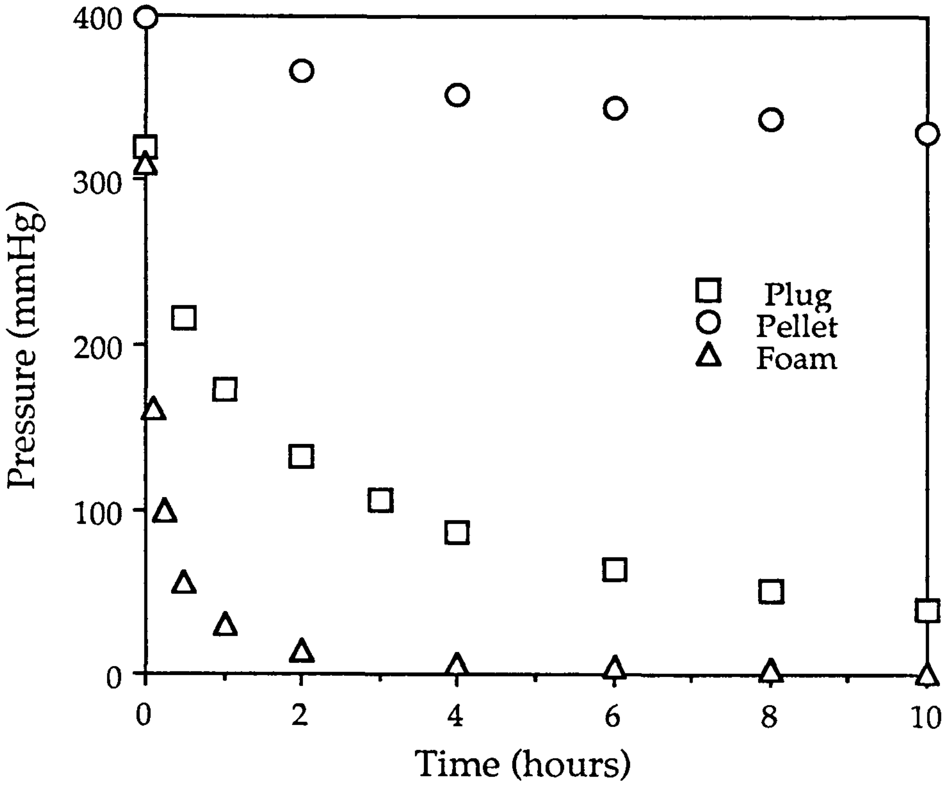
*COD = cyclooctadiene, Py = Pyridine, tcyp = tricyclohexylphosphine.



The 100°C glass transition of the polystyrene domain imparts structural integrity and allows preparation of a variety of interesting fabrications. Specific forms include: a plug - prepared by dissolving polymer and catalyst in dichloromethane and rapidly removing the solvent, the plug is lightly foamed by the solvent evaporation; a foam - prepared by freezing a benzene solution of catalyst and polymer, then freeze-drying, the foam has a oriented open-celled structure; a pellet - prepared by molding a plug at 90°C; a coating - prepared by solvent evaporation or spin coating from a solution of polymer and catalyst. The reactivity of the getter is critically dependent on the method of fabrication as is shown below. Presumably, since the foamed structures have a greater surface area, the reactivities reflect the accessibility of hydrogen to the catalyst.



Graph 4: Relative hydrogen uptake for the three formulations of polymeric getter.

The theoretical capacity of the material is 290 cc per gram of getter. With the exception of the pellet, all fabrications readily exceed 90% of the theoretical uptake capacity. Although the getter is poisoned by carbon monoxide and amines, it is not affected by air or water, and does not produce water upon reacting with hydrogen in air. Unfortunately, the polymer and catalyst lack the sufficient radiation stability to be an effective getter for tritium.

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