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Organic hydrogen getters

Part 1

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A solid unsaturated organic–catalyst combination has been developed which can irreversibly getter hydrogen from closed systems via chemical reaction. The unsaturated organic is 1, 6-diphenoxy-2, 4-hexadiyne or dimerized phenyl propargyl ether (DPPE), and the catalyst is 5% Pd–$CaCO_3$. The structure of DPPE (m.p. 80° C) was verified by infra-red and Raman spectroscopy and by elemental analyses. The compounded getter has been shown to be non-explosive and even when completely hydrogen saturated, non-pyrophoric. Kinetic studies show that the getter reacts with sufficient speed to prevent hydrogen build-up in closed systems containing reactive metals and water. The activation energy for hydrogen uptake was determined to be 9.4 kcal mol^{-1} over the temperature range 22 to 55° C.

1. Introduction

The concentration of hydrogen, if allowed to build up, in closed systems may exceed the normally accepted safety limit of 4% by volume or cause malfunction of electrical components, as well as hydrogen embrittlement of metals.

The removal, or gettering, of hydrogen from closed systems in the past has involved the use of noble metal catalysts in combination with molecular sieves using primarily platinum or palladium. A platinum or palladium molecular sieve can, in the presence of oxygen, effectively getter the hydrogen by converting the molecular hydrogen into water. However, these types of getters are not effective for use in closed systems void of oxygen. Both platinum and palladium form stable hydrides in the absence of oxygen and upon subsequent exposure to the atmosphere are extremely pyrophoric. Therefore, to overcome this difficulty a study was initiated to develop a solid, non-pyrophoric organic hydrogen getter formulation capable of irreversibly removing molecular hydrogen via a chemical reaction from closed systems.

A survey of the literature revealed that the heterogeneous hydrogenation, using a group VIII noble metal catalyst, of an alkyne was the most likely approach in the development of a solid hydrogen getter active at 25° C with the ability of maintaining hydrogen partial pressures in the low ppm range. Although there have been many investigations concerning the heterogeneous hydrogenation of alkynes, most of the studies deal with gas phase reactions using such gases as acetylene [1–5], ethylacetylene [6–8], and methylacetylene [9–11]. Some higher molecular weight compounds containing the triple bond have also been reduced in solution [12–14]. However, at the time this study was initiated, the literature contained no reports covering the neat hydrogenation of solid alkynes.

The acetylenic compound chosen to study the feasibility of using acetylenes in hydrogen getter formulations was phenyl propargyl ether (PPE). Although PPE was easily hydrogenated (neat) over a wide range of hydrogen pressures, the material did not conform to previously established getter requirements (Section 2). First of all, PPE is a liquid, and although it has a low vapour pressure, appreciable migration of PPE can take place at elevated temperatures. Secondly, PPE has a terminal acetylenic, acid hydrogen which can react with certain heavy metal ions, chiefly Ag^+ and Cu^+, to form explosive acetylides.

To overcome these disadvantages, oxidative coupling of two phenyl propargyl ether molecules was used to form 1, 6-diphenoxy-2, 4-hexadiyne (dimerized phenyl propargyl ether–DPPE). This paper describes the preparation and general characterization of DPPE, and a DPPE/5% Pd–$CaCO_3$ hydrogen getter formulation.

2. Hydrogen getter requirements

The following criteria were used in selecting materials for gettering formulations:

(1) both reactants and products should be as chemically inert to their environment as possible except for hydrogen reactivity;

(2) reactants and products should have very low vapour pressures to ensure long term stability;

(3) the forward (gettering) reaction should be irreversible or lead to extremely low hydrogen equilibrium concentrations;

(4) the forward reaction rate should be sufficient to keep the dynamic partial pressure of hydrogen low during corrosion or outgassing in practical systems;

(5) the reacting system should be mechanically convenient to incorporate into various types of systems;

(6) getters should be passive devices requiring no external energy sources for initiation.

A gettering formulation fulfilling these requirements would ensure the irreversible removal of hydrogen without detrimental side reactions.

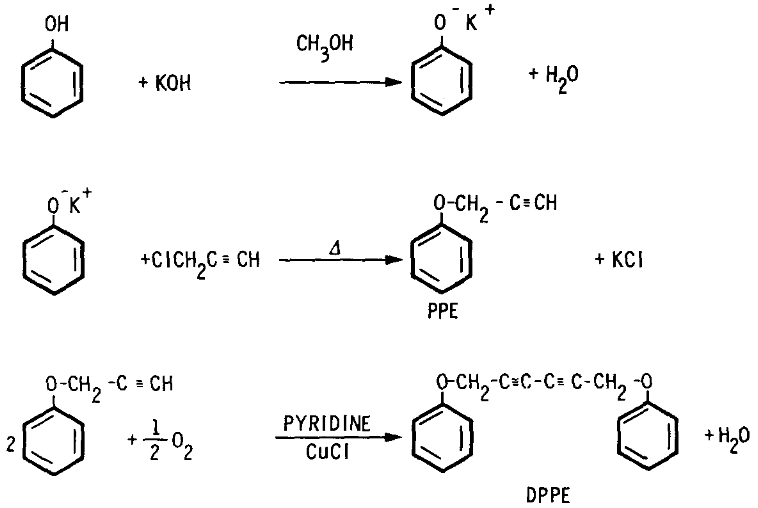
3. Materials and methods

3.1. Materials

The 1, 6-diphenoxy-2, 4-hexadiyne (DPPE) was prepared by the oxidative coupling of phenyl propargyl ether (PPE), which was previously prepared via a Williamson reaction between potassium phenoxide and propargyl chloride. The following procedure was used to prepare 1, 6-diphenoxy-2, 4-hexadiyne [15, 16].

To a 250 ml wide-mouthed Erlenmeyer flask in a water bath at 28°C was added 135 ml acetone, 1 g (0.01 mol) of CuCl and 1.2 g (0.01 mol) of *N*, *N*, *N'*, *N'*-tetramethylethylenediamine. Oxygen was bubbled into the solution with vigorous stirring. Over a 15 min period, 25 g (0.19 mol) of propargyl phenyl ether was added drop by drop to the reaction mixture. After the addition was complete, the reaction was continued for 20 min, then the acetone was evaporated and 20 ml water containing 1 ml concentrated HCl was added. The white solid was filtered off and washed with a small amount of water and dried under vacuum. The yield of DPPE (MP-80° C) from this procedure was 93%.

The overall reactions from the preparative methods are as follows:



The completely reduced form of the heterogeneous catalysts, 5% Pd–$CaCO_3$ and 5% Pd–alumina, were obtained from Strem Chemicals, Incorporated, Danvers, Massachusetts. The catalysts did not receive special treatment prior to being coated with the DPPE.

3.2. Methods

3.2.1. Product characterization

The product structures of PPE and DPPE were verified using a Perkin-Elmer, Model 21, double beam infra-red spectrometer and a Jarrel-Ash,

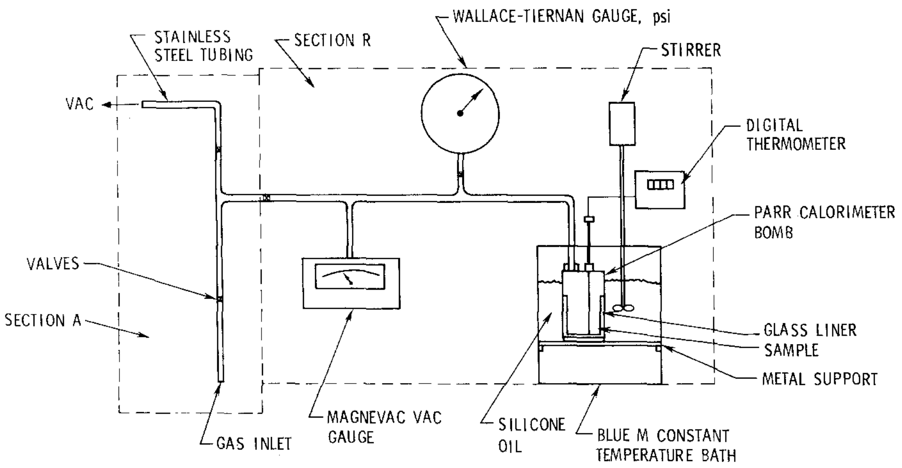


Figure 1 Hydrogenation apparatus.

25-2400, Laser-Raman spectrophotometer.

A small sample of DPPE was quantitatively hydrogenated using 5% Pd–$CaCO_3$, and the thermal properties of the hydrogenated product (HDPPE) were compared to those of DPPE. The thermal analyses were conducted using a DuPont 900 console with the appropriate TGA (thermalgravimetric analysis) and DSC (differential scanning colorimeter) plug-in modules.

3.2.2. Hydrogen getter sample preparation

Samples of varying DPPE/5% Pd–$CaCO_3$ compositions were prepared in order to determine the amount of DPPE required for complete catalyst coverage.

The samples were prepared by first mixing prescribed amounts of DPPE and 5% Pd–$CaCO_3$ together in a glass vessel such that the mixture completely covered the bottom of the vessel. The vessel containing the mixture was then placed into an oven at 85 to 90° C. After the DPPE melted and flowed onto the 5% Pd–$CaCO_3$, the mixture was removed from the oven and the DPPE was allowed to recrystallize at room temperature. The resulting slug of material was then ground into a powder using a mortar and pestle and the powder passing through a 60 mesh sieve was used for further evaluation. A total mix of 5.0 g was used for each DPPE/5% Pd–$CaCO_3$ formulation.

3.2.3. Quantitative and qualitative hydrogenation experiments

The various hydrogen getter formulations were quantitatively hydrogenated in the apparatus diagrammed in Fig. 1. The volume of the apparatus (section R) was measured using a calibrated Vol-u-meter[*] and found to be 465 ml. Hydrogenations were conducted by first placing and uniformly spreading a 0.50 g quantity of a given formulation into the glass liner which was then lowered into the Parr calorimeter bomb. The system was then evacuated and hydrogen introduced to a pressure of 4.83×10^{-2} MPa (7.0 psi) through section A. The total uptake of hydrogen (pressure drop) was followed as a function of time until no further pressure drop was observed.

The DPPE/5% Pd–$CaCO_3$ formulation representing complete catalyst coverage was determined by measuring the temperature rise associated with the initial introduction of hydrogen and subsequential rapid exposure to air, or oxygen, after the system had equilibrated. These temperature rise measurements were used as criteria for catalyst coverage because the heats of formation of palladium hydride (addition of hydrogen) and water (addition of air, or oxygen) are exothermic. These temperature measurements were obtained by modifying the lid of the calorimeter bomb so as to accomodate a digital thermometer.

The qualitative hydrogenation experiments consisted of exposing a 0.50 g sample of each getter formation in a 125 ml Erlenmeyer flask to a hydrogen flow rate of 1.5×10^{-2} litres $\sec^{-1}$ for 2 min. After the 2 min period elapsed, the hydrogen flow was discontinued and each sample was rapidly exposed to the atmosphere. These

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[*] Trade name for Brooks Instrument Company, Incorporated.

experiments allowed the visual observation of each formulation for pyrophoric characteristics, e.g. burning, hot spots, etc.

The remaining portion of this section pertains to the particular DPPE/5% Pd–$CaCO_3$ hydrogen getter system which was chosen for further study. For safety reasons, with respect to pyrophoricity, the formulation chosen for general characterization consisted of 75% DPPE and 25% catalyst (5% Pd–$CaCO_3$). The hydrogen getter system was identified as 75M-60. The 75M means that 75%, by weight, DPPE was coated onto the 5% Pd–$CaCO_3$ from the melt phase, and the number 60 refers to the getter powder being passed through a 60 mesh sieve.

3.2.4. General characterization of the 75M-60 hydrogen getter system

3.2.4.1. Explosive testing. Since acetylenic compounds are generally accepted as materials having a tendency to be explosive, it was necessary to evaluate the potential explosive properties of the properties of the 75M-60 getter formulation. The tests performed on this material were (1) thermal analysis at heating rates of 5, 10, 20 and 50° C min^{-1}, (2) impact sensitivity using a 2 kg weight at a height of 200 cm, (3) spark sensitivity at 0.3, 0.5 and 1.0 J, (4) auto-ignition, (5) response to a high temperature flame using an electric match to ignite an energetic mix of lead mononitroresorcinol and potassium chlorate, and (6) response to a detonation front by a detonating tetryl pellet. The auto-ignition test mentioned above measures the time necessary for a material to explode, ignite, or decompose at some isothermal temperature.

3.2.4.2. Particle size analyses. The particle size analyses on the 75M-60 material were conducted on the Quantimet 720 image analysing computer. Total area and total perimeter measurements were made on 308 particles for the 5% Pd–$CaCO_3$ and on 329 particles for the 75M-60 getter powder. Size distributions using the horizontal Feret (horizontal extent of the feature) and area as sizing parameters were also obtained.

A Jeolco SEM was used to observe the distribution of the 5% Pd–$CaCO_3$ particles in the DPPE matrix.

3.2.4.3. Kinetic study. The kinetic study, as a function of temperature and initial hydrogen pressure, was conducted in the apparatus shown in Fig. 1 using 0.50 g samples of the 75M-60 getter material. The samples were hydrogenated in the same manner as those samples in the quantitative hydrogenation experiments. Initial reaction rates were measured over a temperature range of 22 to 55° C using an initial hydrogen pressure of 0.69×10^{-2} MPa (1.0 psi) and a pressure range of 0.69 to 6.9×10^{-2} MPa (1.0 to 10.0 psi) at 22° C. The activation energy was obtained from an Arrhenius plot over the temperature range investigated.

The rate of weight loss and vapour pressure of the 75M-60 material was measured at 71 ± 1 and 78 ± 1°C using thermogravimetric and mass spectrometric experiments. The samples were heated in a Knudsen cell and the sample weight was monitored with an Ainsworth thermogravimetric balance. The evolving vapour species were continuously monitored from 1 to 100 AMU with an EAI Quad 1210 residual gas analyser.

A second sample composed of 75% by weight DPPE coated (from the melt) onto 5% Pd–alumina was also evaluated at 78 ± 1° C. The alumina system was prepared in the same way as the 75M-60 getter.

The effect of polyethylene bagging upon the kinetics of hydrogen gettering by the 75M-60 material was also briefly studied. The 0.50 g samples of the getter powder were sealed in

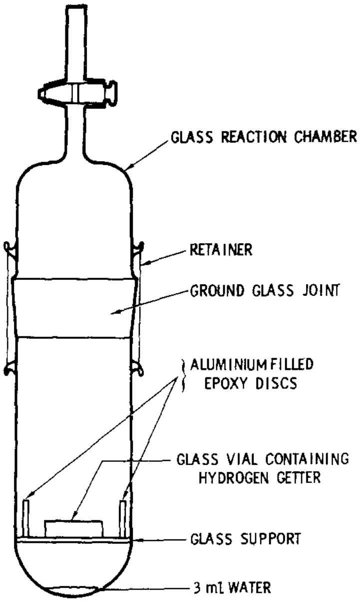

Figure 2 Glass vessel used in closed system experiment.

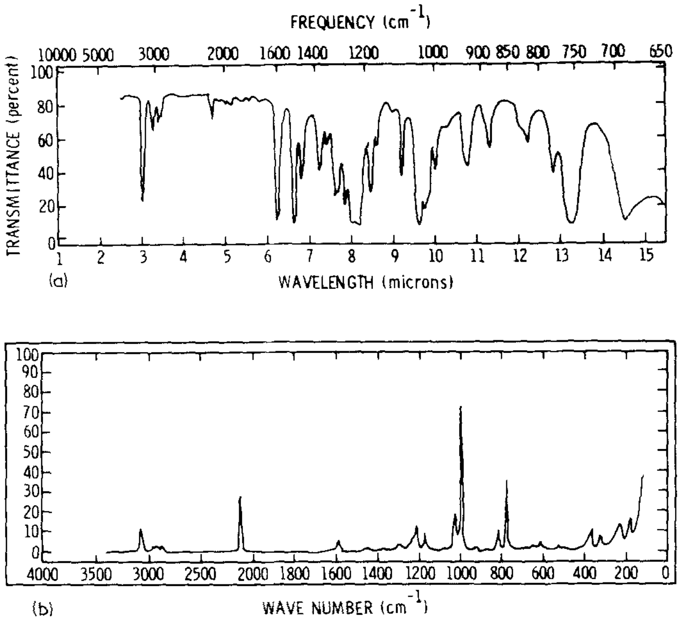

Figure 3 (a) Infra-red and (b) Raman spectra for phenyl propargyl ether.

0.0127 cm thick polyethylene bags (area = 10.08 cm^2), and hydrogenated in the apparatus shown in Fig. 1. The experiments were carried out at initial hydrogen pressures of 1.38×10^{-2} MPa (2.0 psi) and 4.83×10^{-2} MPa (7.0 psi) at 22°C.

3.2.4.4. Closed system evaluation of getter. These experiments were conducted to determine the gettering effectiveness of the 75M-60 material at low partial pressures of hydrogen. The total weight of getter used was 0.30 g and the glass vessel used is shown in Fig. 2.

The hydrogen was generated *in situ* by the reaction of water vapour with aluminium dispersed in epoxy discs at 50° C. A control vessel, no getter present, was used to determine the amount of hydrogen actually being produced. The free volume of both vessels was approximately 460 ml. The hydrogen concentration in both vessels was periodically checked over a 2 month span with a

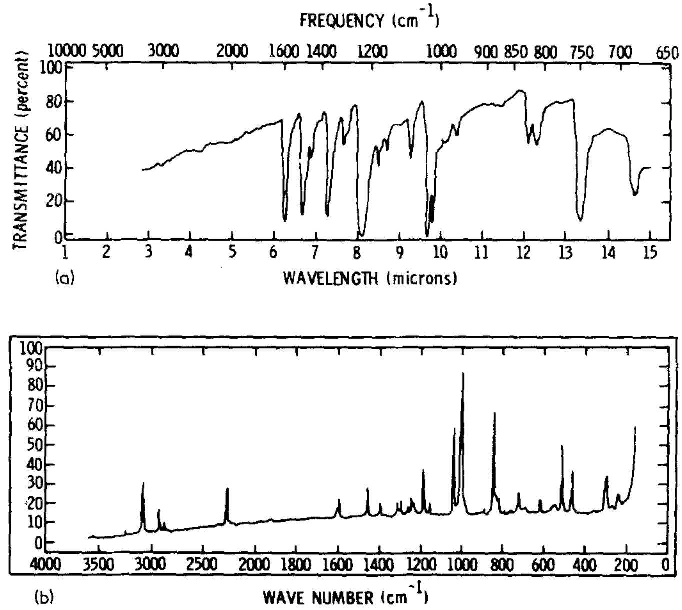

Figure 4 (a) Infra-red and (b) Raman spectra for dimerized phenyl propargyl ether.

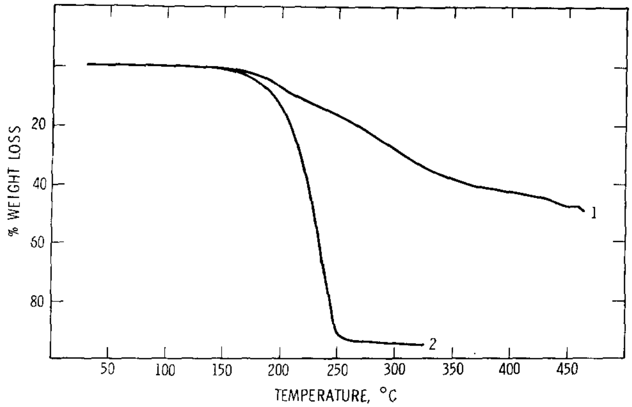

Figure 5 Thermogravimetric analysis: curve 1 is DPPE and curve 2 is completely hydrogenated DPPE (HDPPE).

gas chromatograph capable of detecting 0.5 ppm hydrogen.

4. Results and discussion

4.1. Product characterization

The product structures of PPE and DPPE were vertified using infra-red and Raman spectroscopy and the spectra obtained are shown in Figs. 3 and 4, respectively. The acetylenic CH stretch for PPE is located at 3310 $\mathrm{cm^{-1}}$ and the triple bond stretch at 2120 $\mathrm{cm^{-1}}$. The spectra for DPPE show that the acetylenic CH is no longer present and that the triple bond has shifted to a higher frequency of 2250 $\mathrm{cm^{-1}}$ (doubly substituted acetylene). Also, there are no double bonds present (1650 $\mathrm{cm^{-1}}$) which means that during oxidative coupling the triple bond is not destroyed and only the acetylenic acid hydrogen takes part in the reaction. The results from the carbon, hydrogen, and oxygen (by difference) analyses of DPPE were 82.33% C, 5.35% H, and 12.32% O. The theoretical percentages are 82.41% C, 5.39% H, and 12.20% O.

The results of the thermal analysis of DPPE and HDPPE are displayed in Figs. 5 and 6. The weight loss curves are different for the two materials, with the DPPE affording a 50% residue and the HDPPE only a 5 to 6% residue. The DPPE residue was a black, brittle, glassy material. The difference between the two TGA curves is probably due to the DPPE polymerizing through the triple bonds. This polymerization causes the exotherm observed for DPPE at 200° C (see Fig. 6), and the energy output of the exotherm was 221 cal $\mathrm{g^{-1}}$. As previously stated, DPPE is a white solid, but the HDPPE is a waxy material. The infra-red and Raman spectra for HDPPE are shown in Fig. 7.

4.2. Quantitative and qualitative hydrogenation experiments

The hydrogen uptake curves for the various hydrogen getter formulations are shown in Fig. 8 for the first 60 min of the reaction. The initial hydrogen pressure used for all experiments was 4.83×10^{-2} MPa (7.0 psi), and the percentage (20, 30, 45, etc.) of DPPE used is indicated for each curve. The curves having rather abrupt endings (20 to 60% DPPE) exhibited varying degrees of pyrophoricity, which ranged from being extremely pyrophoric (20% DPPE) to only slightly

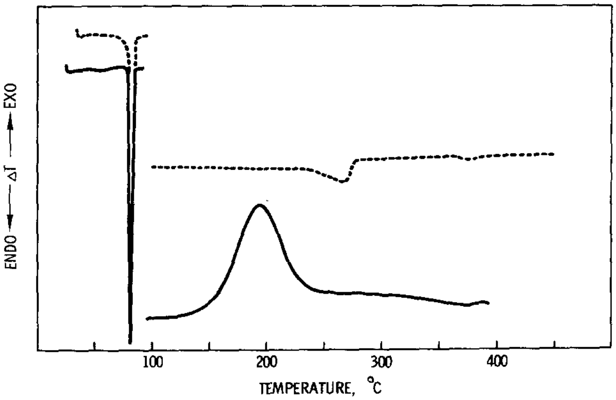

Figure 6 Differential scanning calorimetry: the solid line is DPPE and the dashed line is HDPPE.

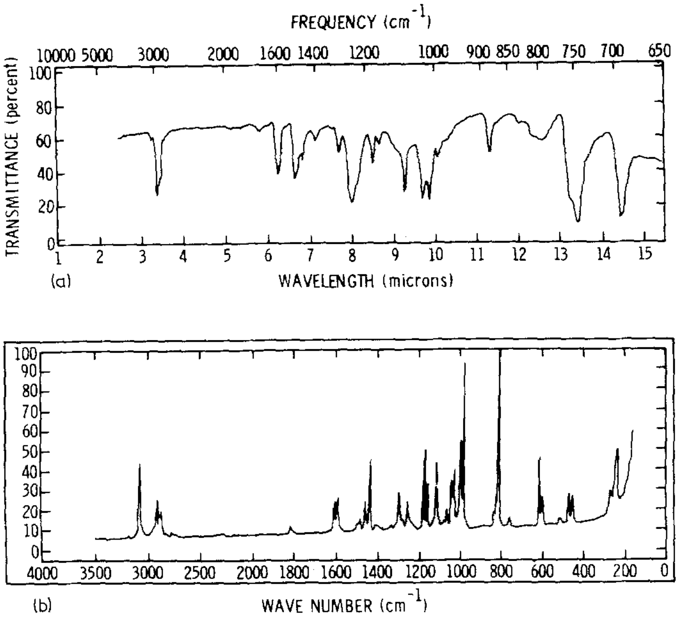

Figure 7 (a) Infra-red and (b) Raman spectra for completely hydrogenated dimerized phenyl propargyl ether.

warm with no visual signs of buring (60% DPPE). When using higher than 60% DPPE the hydrogen uptake was more gradual with reduction in the initial reaction rate (Fig. 9a).

As seen in Fig. 9b, the 65% DPPE–35% catalyst mix was the initial formulation at which no temperature rise was observed due to the addition of hydrogen or air. The 65% DPPE–35% catalyst mix showed no signs of being pyrophoric. This 65% DPPE formulation is not considered to be representative of monomolecular coverage of the catalyst but rather the amount of DPPE required to protect the catalyst from rapid oxidation upon exposure to oxygen. The ability of the DPPE to wet the catalyst would depend upon the number and size of pores and internal capillaries associated with the catalyst, as well as the viscosity of the molten DPPE. Also, since the 65% DPPE formulation is not pyrophoric, there is enough

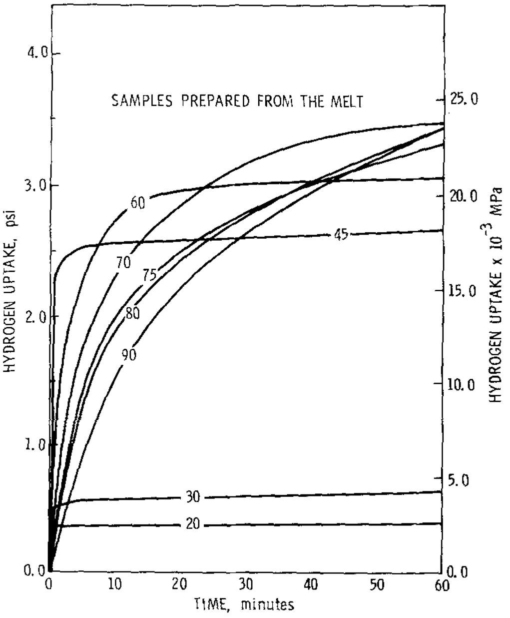

Figure 8 Hydrogen uptake as a function of the DPPE/5% Pd–$CaCO_3$ formulation.

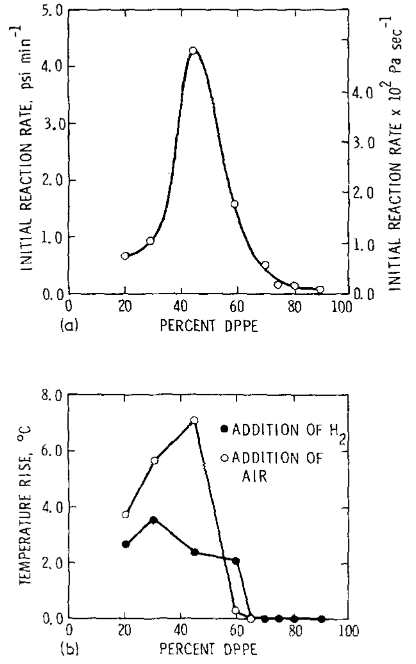

Figure 9 The effect of getter formulation on initial reaction rate (a) and temperature rise measurements (b).

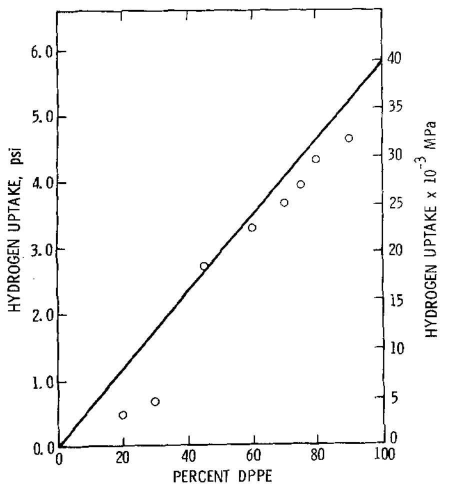

Figure 10 Totoal hydrogen uptake as a function of the DPPE/5% Pd–CaCO$_3$ formulation.

excess DPPE to allow grinding without exposing the catalyst. The temperature rise data were corrected for the temperature of the hydrogen gas and air by conducting control (no DPPE) experiments using an equal volume of CaCO$_3$.

The solid line in Fig. 10 represents the stoichiometric uptake of hydrogen, based on the DPPE concentration, while the open circles show the actual amount of hydrogen taken up by the various formulations. The 0.50 g sample of the 75% DPPE getter mix took up 3.94 psi hydrogen, which is equivalent to 224 ml (STP)/g getter. The low uptake of hydrogen by the formulations containing less than 40% DPPE probably is a result of polymerization and evaporation during the initial exotherm.

The 75M-60 getter formulation was then exposed for 10 min to a hydrogen flow rate of 1.0 litre min^{-1} followed by exposure to pure oxygen at the same flow rate. The sample was not pyrophoric. The getter mix was also half hydrogenated at an initial hydrogen pressure of 2.76×10^{-2} MPa (4.0 psi). The excess hydrogen was pumped out of the system and 6.89×10^{-3} MPa (1.0 psi) pure oxygen was introduced into the reaction vessel. No temperature rise was observed when adding pure oxygen which agrees with the results obtained upon the addition of air after the sample had been completely hydrogenated.

4.3. General characterization of the 75M-60 hydrogen getter system

4.3.1. Explosive testing

The results of this testing showed that the 75M-60 getter formulation would not present the slightest explosive hazard under ordinary conditions. For example, the 75M-60 formulation gave no indication of sensitivity to an impact stimulus at a height of 200 cm using a 2 kg weight, and during the thermal analysis and auto-ignition tests the material did not explode, or ignite, but rapidly decomposed. Exposure to the high temperature flame resulted in the DPPE melting and charring. Therefore, no self-propagation or buring resulted from the flame front. The results of the detonation front tests showed sugar having a greater response than the 75M-60, and no reaction was indicated during the spark sensitivity tests. The results of these explosive testing techniques allow classification of the 75M-60 hydrogen getter formulation as not explosive.

4.3.2. Particle size analysis

The results for the measurements based on the

TABLE I Data for particle size analysis of 5% Pd–CaCO$_3$ and 75M-60

Slide preparation	5% Pd–CaCO$_3$ Evaporated alcohol suspension		75M-60 Dry powder	
No. of particles	308		329	
Mean area (μm^2)	28		1050	
Mean perimeter (μm)	18		97	
Mean perimeter/area (μm^{-1})	0.65		0.10	
Distribution based on horizontal feret diameter (μm)	0.0 – 0.6	16	0.0 – 1.2	9
	0.6 – 1.7	14	1.2 – 11.8	119
	1.7 – 3.4	66	11.8 – 35.4	117
	3.4 – 4.5	32	35.4 – 70.8	58
	4.5 – 5.6	39	70.8 – 105.2	9
	5.6 – 7.3*	60	106.2 – 118.0	2
	7.3 – 9.5*	61	118.0 – 236.0	14
	9.5 – 11.2*	20	236.0 – 354.0	1

* Probably 90% or more clusters.

TABLE II Data for area sizing distribution of 75M-60

Area (μm^2)	Approximate diameter (assume circular) (μm)	75M-60 particles
0 – 28	0 – 6	61
28 – 144	6 – 14	81
144 – 288	14 – 19	45
288 – 432	19 – 24	17
432 – 576	24 – 27	21
576 – 2880	27 – 60	42
2880 – 5760	60 – 86	4
> – 5760	> – 86	4
Total no. of particles	275	
Mean area (μm^2)	677	
Mean perimeter (μm)	82	
Mean perimeter/area (μm^{-1})	0.12	

TABLE III Initial reaction rate (R_I) as a function of temperature* and pressure†

Temperature (° C)	$R_I \times 10^{-6}$ (mol sec^{-1} g^{-1})	Pressure MPa (psi)	$R_I \times 10^{-6}$ (mol sec^{-1} g^{-1})
22.34	3.01	6.89×10^{-3} (1.0)	2.80
32.71	5.60	1.38×10^{-2} (2.0)	3.15
39.31	7.33	2.07×10^{-2} (3.0)	7.20
44.82	9.05	3.17×10^{-2} (4.6)	10.11
55.17	13.78	4.83×10^{-2} (7.0)	12.32
		6.89×10^{-2} (10.0)	23.17

* Initial hydrogen pressure = 1.0 psi.
† Conducted at 22° C

horizontal Feret are tabulated in Table I. Particles of the 5% Pd–$CaCO_3$ tend to cling together, which makes it difficult to prepare a slide void of agglomerations by conventional techniques. As a matter of fact, when viewed at high magnification (≈ X1000), most particles greater than 5 to 6 μm are indeed clusters. Clusters up to ≈ 48 μm diameter were observed but most of these were broken up by mechanical agitation of the suspension before pouring onto the slide. The areas viewed on this slide had no clusters with horizontal Feret diameter in excess of ≈ 12 μm.

The mean ratio of horizontal Feret to perimeter for all of the 75M-60 particles is 0.30. The majority (92%) of the particles have horizontal extents which fall between approximately 1 and 100 μm. A second distribution using area as size parameter in this range is given in Table II.

The scanning electron micrographs of the 5% Pd–$CaCO_3$ catalyst and 75M-60 getter formulation, before and aftering grinding, are presented in Fig. 11. with the brighter spots being 5% Pd–$CaCO_3$ particles. The micrographs of the catalyst show how the 5% Pd–$CaCO_3$ particles cling together while the remaining micrographs depict areas of DPPE almost void of any 5% Pd–$CaCO_3$. This is to be expected since excess DPPE is being used in the getter formulation.

4.3.2. Kinetic study

All the initial reaction rates (the first minute) over the temperature and pressure ranges studied are listed in Table III. A linear relationship is obtained from a plot of initial hydrogen pressure versus initial reaction rate which indicates the reaction kinetics are first order with respect to hydrogen.

A linear Arrhenius plot–log R_I versus $1/T$ (10^{-3} K^{-1})–over the temperature range investigated gave an activation energy of 9.4 kcal mol^{-1}.

The isothermal weight loss behaviour for the 75M-60 powder and the sample using 5% Pd–alumina as a catalyst is summarised in Fig. 12. The rate of weight loss for the 75M-60 sample is 0.29 ± 0.01 mg hr^{-1} and the rate for the DPPE 5% Pd–alumina sample is 0.26 ± 0.01 mg hr^{-1} at 78° C. These data lead to a very small difference in vapour pressure as calculated from the Knudsen equation, 1.53×10^{-7} MPa (1.51×10^{-6} atm) for

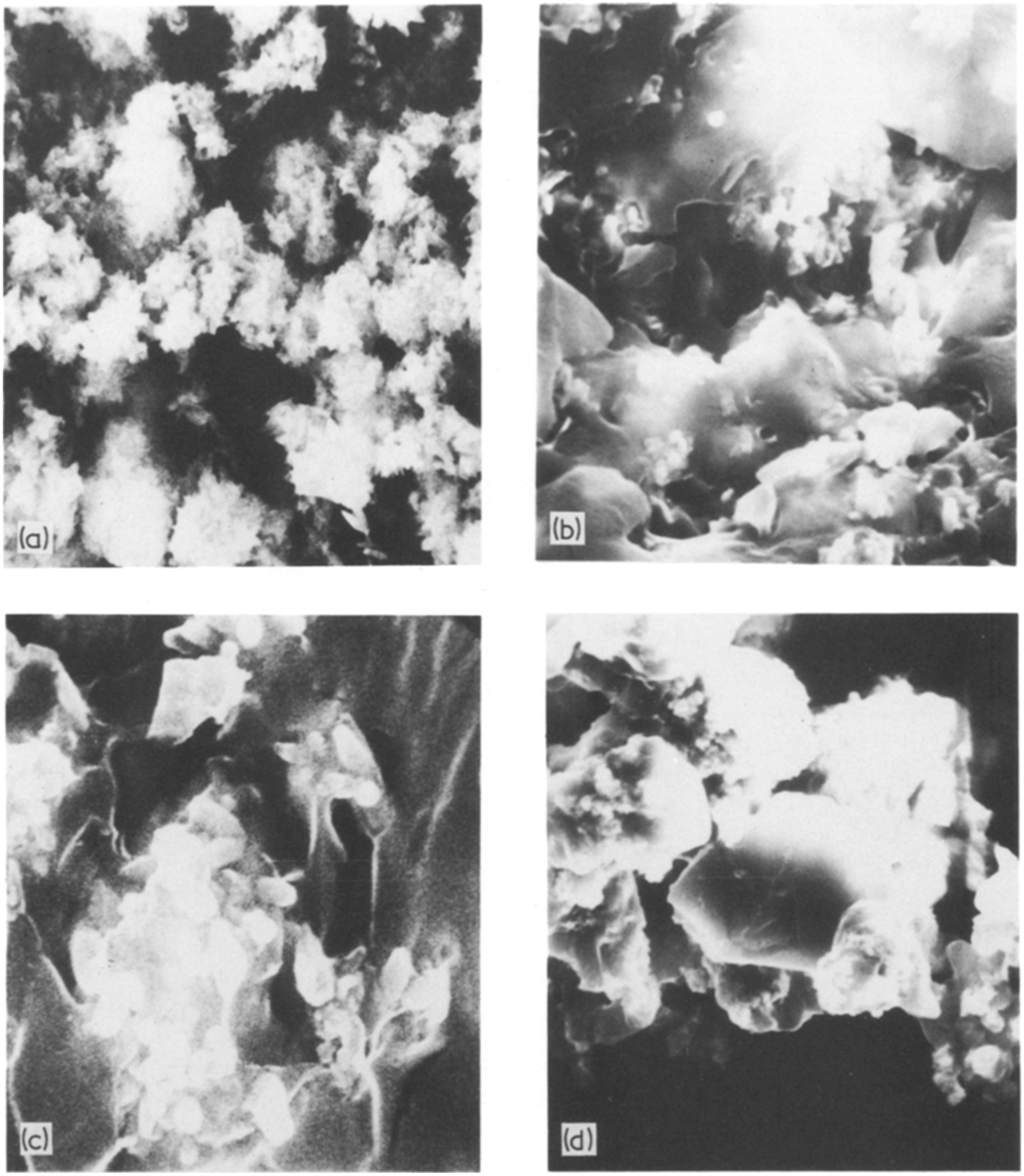

Figure 11 Scanning electron micrographs of (a) 5% Pd–$CaCO_3$, × 3000; (b) 75M-60 sample prior to grinding, × 3000; (c) as (b) × 10 000; (d) 75M-60 powder × 1000.

the 75M-60 material and 1.40×10^{-7} MPa (1.39×10^{-6} atm) for the system using 5% Pd–alumina.

No unusual features were noted except for an increase in the CO_2 peak as the DPPE melted away from the 5% Pd–$CaCO_3$ catalyst (79 to 80° C). This is not surprising since calcium carbonate is not thermodynamically stable. No evolution of CO_2 was observed from the sample using 5% Pd–alumina.

Fig. 13 shows the effect of packaging the 75M-60 getter in polyethylene bags. The hydrogen uptake by the packaged samples was quantitative and the reaction kinetics appear to be controlled by the rate at which hydrogen permeates the polyethylene. The number interrupting the curves

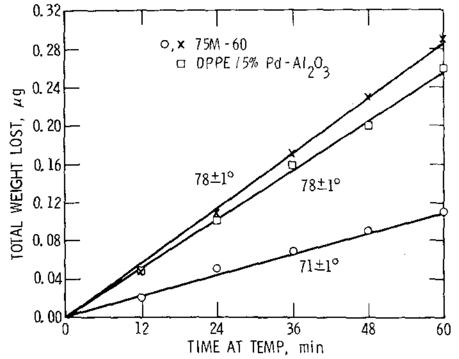

Figure 12 Isothermal weight loss of 75M-60 and DPPE coated onto 5% Pd–alumina.

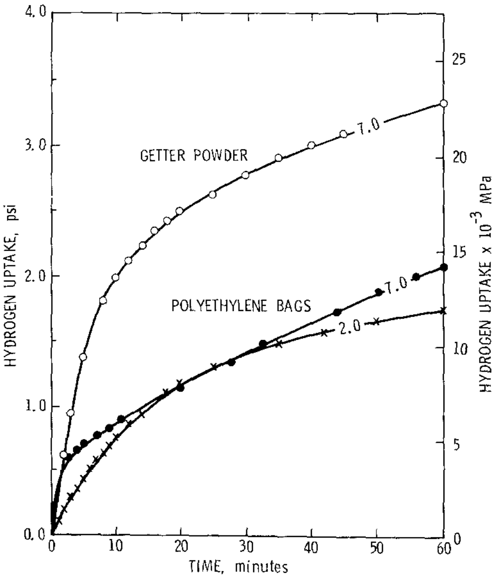

Figure 13 The effect of packaging on gettering efficiency.

represents the initial hydrogen pressure (psi) used for each experiment.

4.3.4. Closed system evaluation of getter

Using the reaction of aluminium filled epoxy with water, the hydrogen concentration, after 1 week, in the control vessel was 50 ppm and 800 ppm at the end of the 2 month period. In the vessel containing the 75M-60 hydrogen getter, no hydrogen was detected during the course of the experiment which means the hydrogen concentration was maintained below 0.5 ppm.

This experiment also showed that the getter was not affected by the presence of air or water vapour.

5. Conclusions

This study has demonstrated the use of a solid unsaturated organic (DPPE)–catalyst (5% Pd–$CaCO_3$) combination in gettering molecular hydrogen irreversibly from closed systems via a chemical reaction.

This material can be used as a powder or be packaged in a bag through which hydrogen can permeate. This allows the organic getter to be utilized in many ways, regardless of the configuration of the free volume from which hydrogen is being moved. Although the toxicity of the getter powder is not known, the material is not a thermal or explosive hazard. The distinct advantage of this organic getter is that upon previous exposure to only hydrogen, it is not pyrophoric when rapidly exposed to air or oxygen. This is true whether the material is only half or completely hydrogenated which indicates that the DPPE and the products of hydrogenation stay in contact with and adequately cover the catalyst surface.

The amount of DPPE used in the formulation of the 75M-60 getter is in excess of that required to cover the catalyst and yet the hydrogen uptake by the material is quantitative. This can be explained by an increase in the mobility of the organic on the catalyst surface caused by a change in the physical state of the DPPE [17]. The DPPE, as it is being hydrogenated, appears to form a eutectic which has a minimum melting point near 25° C with the final product of hydrogenation being a waxy solid.

A study has been initiated to look into the kinetics and mechanism of hydrogenation of the DPPE–Pd catalyst system. Further studies are under way to develop hydrogen getter systems with higher molecular weight acetylenic compounds and polymers which afford lower vapour pressures and higher operating temperatures.

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References

1. G. C. BOND and P. B. WELLS, *J. Catalysis* **4** (1965) 211.
2. *Idem, ibid* 5 (1965) 65.
3. *Idem, ibid* 5 (1966) 419.

4. *Idem, ibid* **6** (1966) 397.
5. *Idem, ibid* **12** (1968) 157.
6. R. S. MANN and K. C. KHULBE, *ibid* **10** (1968) 401.
7. *Idem, ibid* **13** (1969) 25.
8. *Idem, ibid* **17** (1970) 46.
9. R. S. MANN and S. C. NAIK, *Canad. J. Chem.* **45** (1967) 1023.
10. R. S. MANN and K. C. KHULBE, *ibid* **45** (1967) 2755.
11. *Idem, ibid* **46** (1968) 623.
12. P. H. EMMETT, Ed., "Catalysis, Volume III: Hydrogenation and Dehydrogenation" (Reinhold, New York, 1955).
13. K. N. CAMPBELL and B. K. CAMPBELL, *Chem. Rev.* **31** (1942) 77.
14. L. M. BERKOWITZ and P. N. RYLANDER, *J. Org. Chem.* **24** (1959) 708.
15. H. CHANAN, private communication.
16. A. S. HAY, *J. Org. Chem.* **27** (1961) 3320.
17. W. E. SMITH, private communication.

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