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Thermochemical properties of the hydrogen getter DEB

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Abstract

Vapor pressures of the hydrogen getter 1,4 bis(phenylethynyl)benzene (DEB), together with two of its derivatives namely DEB mixed with carbon-supported Pd (DEB–Pd/C) and hydrogenated DEB–Pd/C, are measured from room temperature to the melting temperature (179°C). The corresponding thermodynamic information, such as the enthalpy of vaporization, boiling point, and the deviation from ideal solution behavior of DEB–Pd/C, has been derived from the vapor pressure–temperature relationships. In addition, the hydrogenation kinetics of DEB–Pd/C (powder form and rod-like) has also been investigated at a fixed pressure of 13.3 Pa (0.1 Torr) and at four temperatures, 21°C, 35°C, 45°C and 55°C. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Hydrogen getters have been studied extensively in many areas of concern, such as hydrogen corrosion of nuclear reactor materials, hydrogen effects on electronic components and electrical assemblies and safety concerns for hydrogen as an explosive hazard [1,2]. Among various getters, the organic hydrogen getters are usually a blend of an organic acetylenic compound with a metal catalyst (e.g. Pd) on a carbon substrate

$$—C\equiv C— + 2\,H_2 \xrightarrow{Pd/C} —CH_2—CH_2—$$

The major advantage of the organic getters lies not only in their rapid and irreversible hydrogen uptake, but also in their substantial hydrogen absorption capabilities (per unit weight). Early organic getters, such as 1,4-diphenyl butadiyne (DPB) and 1.6-diphenoxy-2, 4-hexadiyne (DPPE), have only limited applications due to their low melting points (87°C and 80°C, respectively). Vapor pressures of these getters, however, have been reported by Garza and Colmenares [3].

The hydrogen getter discussed here, DEB, known for its higher hydrogen absorption capacity, has been shown to have higher operating temperatures due to its higher melting point (179°C). In the present work, the vapor pressures of three types of DEB, namely pure DEB, DEB mixed with carbon-supported Pd (DEB–Pd/C), and hydrogenated DEB–Pd/C (all in fine powder form), are measured from room temperature to the melting temperature using a thermogravimetric method. In addition, the hydrogenation kinetics of two types of DEB–Pd/C, i.e., in powder form and in rod-like form (compacted from powder into rods 3mm in diameter and 3 mm in length), have also been investigated at a fixed pressure of 13.3 Pa (0.1 Torr) and at four temperatures, 21°C, 35°C, 45°C and 55°C.

2. Experimental

Vapor pressure and hydrogen uptake measurements were carried out in a Thermogravimetric Analyzer (TGA) which consists of a Cahn electrobalance (model C1000) installed in an ultra-high vacuum system equipped with a liquid nitrogen trapped turbo molecular pump. The system has a base pressure in the low 10^{-6} Pa range. Hydrogen uptake of DEB was carried out at a fixed hydrogen pressure supplied from an ultra-high purity hydrogen source. Weight change of the sample and the temperature of the reaction chamber were monitored as a function of time by a data acquisition system (LABVIEW) using a computer. The Knudsen

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technique was used to obtain the vapor pressure. Pure aluminum was used to construct the Knudsen cell because it will not react with the specimen both in vacuum and in the hydrogen environment at the temperatures of interest. The cell (ID = 9.6 mm, Height = 10 mm) was initially filled with DEB (~200 mg), which was covered with a very thin lid having an orifice 0.5 mm in diameter. For hydrogen uptake measurements, the lid was removed to provide more surface area accessible for the hydrogen absorption reactions.

3. Results and discussion

3.1. Vapor pressures of DEB, DEB–Pd/C, and hydrogenated DEB–Pd/C

The Knudsen equation was used to calculate the vapor pressure from the weight loss.1

$$P = 3.8 \times 10^{-2} \frac{\mathrm{d}w}{\mathrm{d}t} \sqrt{\frac{T/M}{A}}, \tag{1}$$

where P is vapor pressure in Pascal, A is the cell orifice area (cm^2), M is the molecular weight of the getter ($M_{\mathrm{DEB}} = 278$) in g/mole, T is the temperature in K and dw/dt is rate of the weight loss in mg/min.

Vapor pressure data (in Pascal) of unsaturated DEB, DEB–Pd/C, and hydrogenated DEB–Pd/C are calculated using Eq. (1) with the corresponding values of dw/dt measured directly from the TGA at various temperatures. A least square fits to these data, shown in Fig. 1, yield the following pressure–temperature relationships:

$$\text{DEB(pure)}: \log(P) = 16.1 - \frac{7.1 \times 10^3}{T(K)}, \tag{2}$$

$$\text{DEB–Pd/C}: \log(P) = 16.4 - \frac{7.5 \times 10^3}{T(K)}, \tag{3}$$

$$\text{Hydrogenated-DEB–Pd/C}: \log(P) = 13.9 - \frac{5.7 \times 10^3}{T(K)}. \tag{4}$$

The enthalpy of sublimation of pure DEB, DEB with Pd/C, and hydrogenated DEB–Pd/C derived directly from Eqs. (2)–(4), is −135.8 kJ/mol, −143.4 kcal/mol and −109.1 kJ/mol, respectively. An extrapolated boiling point (defined as the temperature where the vapor pressure reaches one atmosphere) of 639 K was obtained for both pure DEB and hydrogenated DEB–Pd/C using Eqs. (2) and (4), even though vapor pressures of the latter measured are higher in the temperature range studied. In addition, Fig. 1 also demonstrates that the hydrogenated DEB–Pd/C exhibits the highest vapor pressure among these three types of DEB at a fixed temperature.

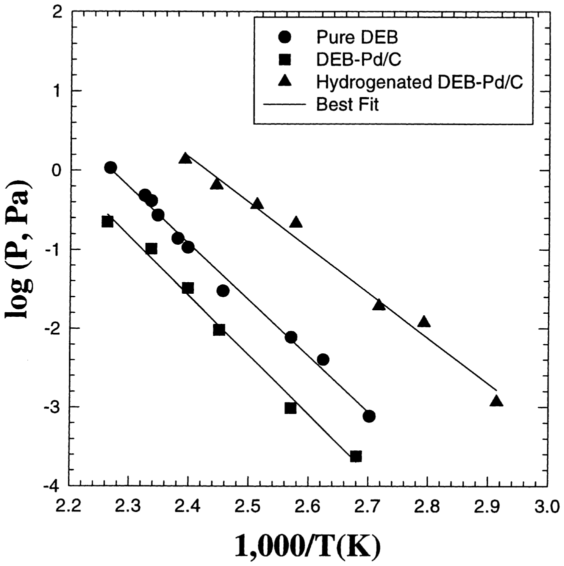

Fig. 1. Comparison of the vapor pressure of unsaturated DEB (solid circle), DEB–Pd/C (solid square) and hydrogenated DEB–Pd/C (solid triangle) measured from an aluminum Knudsen cell with TGA.

3.2. Interaction of Pd/C with DEB

DEB–Pd/C, DEB mixed with carbon-supported Pd, was prepared from 75 wt% of pure DEB (from KEMEX Lab, Ohio) mixed with 25 wt% of carbon–Pd mixture. There is 5 wt% of Pd in this carbon–Pd mixture. The TEM picture in Fig. 2(a) shows that these Pd clusters have a diameter of ~5 nm in diameter and are distributed uniformly in the carbon matrix. Fig. 2(b) is an electron diffraction of one of the Pd clusters, which shows a crystalline-like structure.

It is assumed that DEB–Pd/C can be treated as a pseudo-binary solution consisting of DEB (termed as DEB*) and carbon-supported Pd (termed as Pd/C). The vapor pressure data of pure DEB and DEB–Pd/C can thus be used to evaluate the activity of DEB* in DEB–Pd/C since

$$P_{\mathrm{DEB\text{–}Pd/C}} = P_{\mathrm{DEB}^*} + P_{\mathrm{Pd/C}} \approx P_{\mathrm{DEB}^*},$$

since Pd/C has negligible vapor pressures at the temperatures of interest. Therefore

$$a_{\mathrm{DEB}^*} = \gamma_{\mathrm{DEB}^*} x_{\mathrm{DEB}^*} = \frac{P_{\mathrm{DEB}^*}}{P_{\mathrm{DEB}}} \approx \frac{P_{\mathrm{DEB\text{–}Pd/C}}}{P_{\mathrm{DEB}}}, \tag{5}$$

where x_{DEB^*} is the mole fraction of DEB in DEB–Pd/C and γ_{DEB^*} is the corresponding activity coefficient. If this DEB–Pd/C solid solution behaves like an ideal solution,

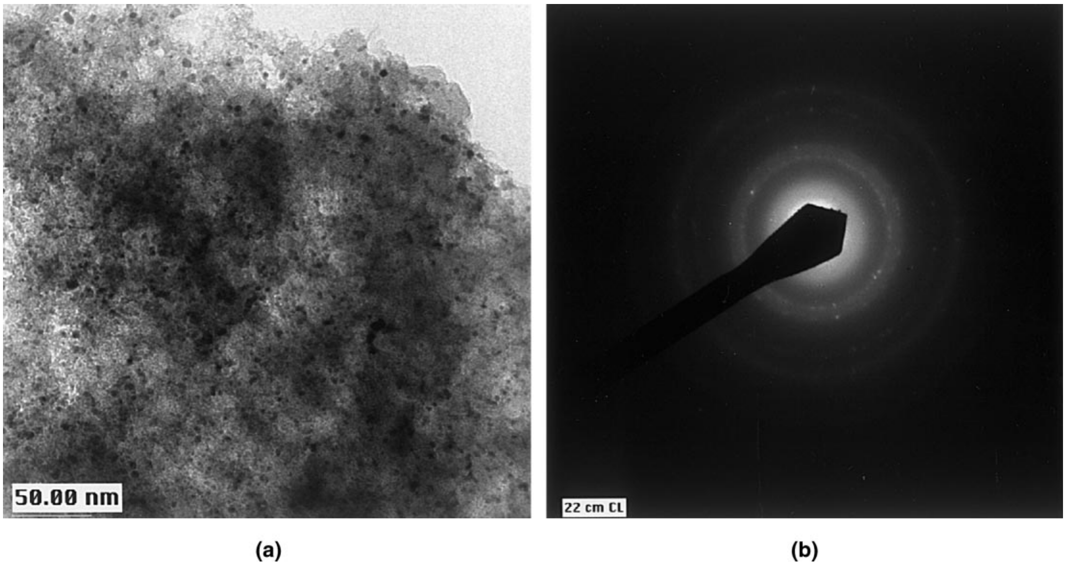

Fig. 2. (a) TEM picture of carbon-supported Pd (~5 nm in diameter, black spots) and (b) Electron diffraction of a Pd cluster.

the value of a_{DEB^*} should be equal to x_{DEB^*}. However, a_{DEB^*} obtained from Eq. (5) ranges from 0.1 to 0.25 ($P_{DEB\text{–}Pd/C} \approx 0.1 \sim 0.25\ P_{DEB}$, as shown in Fig. 1), which is larger than (~0.1) calculated using the mixing recipe given in the beginning of this section. Therefore, γ_{DEB^*} computed using Eq. (5) is larger than unity. Thermodynamically [4], this implies that there appears to be a repulsive interaction between Pd/C and DEB, which renders the vapor pressure of DEB* higher than that predicted from the ideal solution model.

3.3. Hydrogen uptake of unsaturated DEB–Pd/C in 13.3 Pa hydrogen

200 mg of unsaturated DEB–Pd/C was placed inside the aluminum crucible previously used in the vaporization measurements except that the lid was now removed. The specimen was pre-baked in vacuum at 55°C for at least 10 h to remove any water vapor previously adsorbed. The complete removal of the water adsorbed was verified from the weight change signal observed. Baking at temperatures higher than 55°C appears to conglomerate the polymer, which tends to reduce the surface area available for hydrogen uptake. 13.3 Pa (0.1 Torr) of high purity hydrogen was introduced to the reaction chamber at a fixed temperature and the weight change of the specimen was monitored during the experiment. The temperature variation of the reaction chamber was controlled within 0.1°C.

Olander and Balooch [5] measured that the gassification of graphite with hydrogen is greatly enhanced by the presence of platinum. Similar to platinum, palladium is also well known for its catalytic capability in dissociating molecular hydrogen. Therefore, it is suspected that palladium will increase the gassification of the carbon in the Pd/C mixture. Resulting in a weight loss, this effect, however, has not been taken into account in the following analysis due to the lack of available data.

The hydrogen absorption of 200 mg of DEB–Pd/C powder in 13.3 Pa H_2 at 45°C is plotted in Fig. 3. Two competitive processes, i.e., hydrogen uptake that results in the weight gain and vaporization of partially saturated DEB–Pd/C which results in the weight loss, occurred simultaneously in this experiment. In this figure, the weight change signals reached a maximum at about 10 h before it started to decrease. This implies that the vaporization of partially saturated DEB–Pd/C overwhelms the hydrogen uptake after the maximum. It has been demonstrated from the previous section that the vaporization of DEB–Pd/C saturated with hydrogen increases substantially compared with that of unsaturated DEB–Pd/C. In addition, the hydrogen uptake slowed down at the end of the experiment due to the saturation of the specimen.

The weight change of DEB in Fig. 3 during 20–70 h period shows a pattern that the slopes in vacuum and in H_2 repeated itself (independent of time). This implies that vaporization of this specimen during this interval is independent of hydrogen concentration. The reliable data for the rate of hydrogen uptake, however, must take into account the effect of vaporization during the hydrogen absorption. Therefore, the absorption rate calculated using Fig. 3 can be obtained by subtracting the (negative) weight change slope in vacuum (average of three linear curves in Fig. 3) from the weight change slope in H_2 environment (average of two linear slopes in

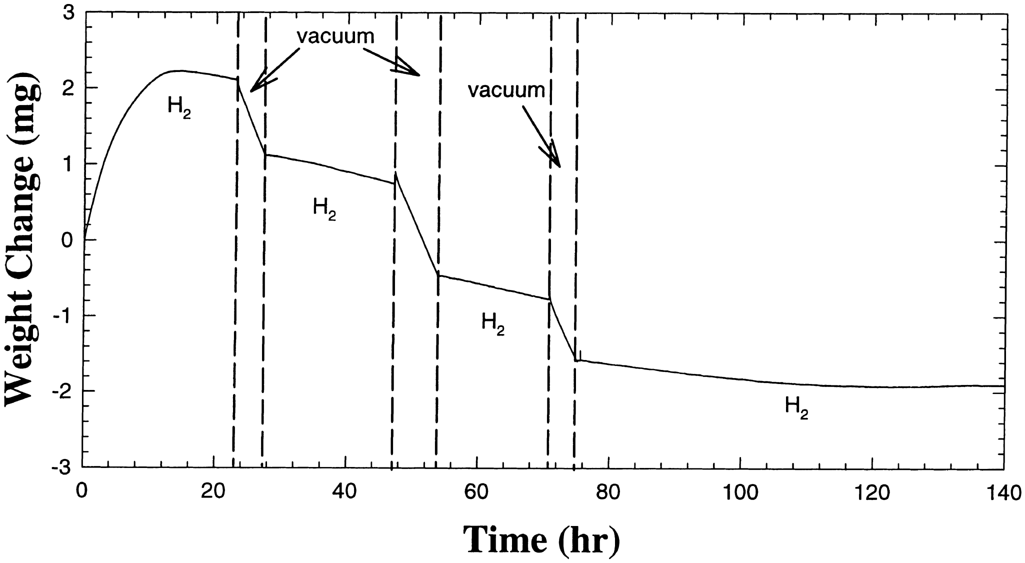

Fig. 3. Hydrogen uptake of 200 mg of DEB–Pd/C (powder form) in 13.3 Pa H_2 and in vacuum at 45°C.

the same figure). The results obtained this way from four temperatures (21°C, 35°C, 45°C, and 55°C), shown as solid circles, are plotted in Fig. 4. The hydrogen absorption rate of DEB–Pd/C at 13.3 Pa (in units of $\mathrm{ngH_2}$/mgDEB–Pd/C/s) can therefore be calculated from the linear regression of the corresponding data in this figure, which yields

$$\ln\left(\frac{\Delta w}{\Delta t}\right) = 3.95 - \frac{1.41 \times 10^3}{T}. \tag{6}$$

The enthalpy of hydrogen absorption estimated from the equation above equals −11.6 ± 0.7 kJ/mole.

In contrast, the hydrogen uptake of 180 mg of unsaturated DEB–Pd/C in rod-like form at 55°C and 13.3 Pa H_2, plotted in Fig. 5, shows little difference in the weight change rate between H_2 environment and vacuum. This implies that hydrogen uptake rate for rod-like DEB–Pd/C is negligible compared with that of the

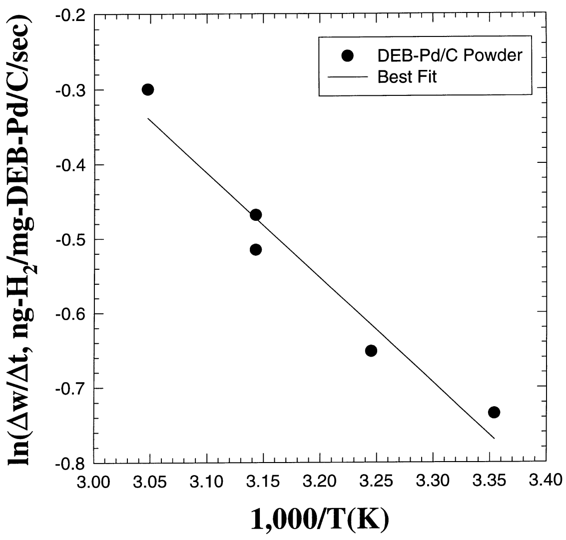

Fig. 4. Hydrogen uptake rate of DEB–Pd/C (powder form) in 13.3 Pa H_2 at 21°C, 35°C, 45°C, and 55°C.

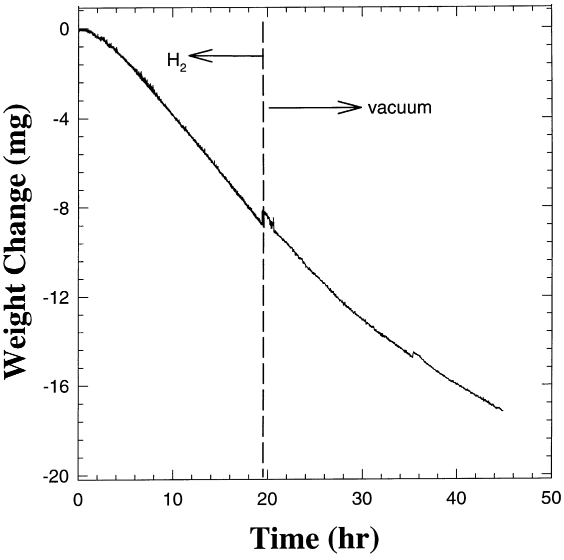

Fig. 5. Hydrogen uptake of 180 mg of the rod-like specimens of unsaturated DEB–Pd/C in 13.3 Pa H_2 and in vacuum at 55°C.

powder form of DEB–Pd/C, which could be attributed to the reduction of surface area available for the former.

4. Summary

Vapor pressures of pure DEB, DEB mixed with carbon-supported Pd (DEB-Pd/C), and hydrogenated DEB–Pd/C, are investigated from room temperature to the melting temperature (179°C). The results show that the vapor pressure of hydrogenated DEB–Pd/C is the highest. The vapor pressure of DEB–Pd/C is higher than that predicted by the ideal solution model, which implies a positive (repulsive) interaction during the mixing of carbon-supported Pd with DEB in forming DEB–Pd/C. In addition, the enthalpy of vaporization and the boiling point of DEB and DEB–Pd/C are derived from the vapor pressure–temperature relationships obtained experimentally. The hydrogen uptake rate of DEB–Pd/C in powder form has been found to be substantial than that in rod-like form probably due to the reduction of surface area available for the latter.

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