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Hydriding kinetics of an organic hydrogen getter-DPB

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Abstract

The hydriding rate of DPB (diphenyl butadiyne/25% C (1% Pd)) organic hydrogen getter has been measured at 17 °C over the range of 10^{-6} to 10^{-11} mol H (g DPB)$^{-1}$ s^{-1}, H_2 pressure 100–0.1 Pa, reaction extent 0–29 mmol H (g DPB)$^{-1}$ and described by an algebraic model.

Keywords: Hydrogen absorbing materials; Corrosion; Catalyst; Kinetics; Gas–solid reactions

1. Introduction

The aging of systems containing hydrogenous materials is often accompanied by the gradual production of hydrogen gas that is a result of the decay of environmental gases and the degradation of organic materials. In particular, the oxygen, water, hydrogen "equilibrium" is affected by the removal of oxygen due the oxidation of metals and organic materials. This shift of the above "equilibrium" towards the formation of hydrogen gas, particularly in crevices, may eventually reach an explosive level of hydrogen gas or degrade metals by hydriding them. The latter process is generally delayed until the oxidizing species are significantly reduced or until relatively high H_2 pressures are reached. Organic hydrogen getters produced by Honeywell Federal Manufacturing and Technologies, Kansas City Plant have proven to be a very effective means of preventing H_2 accumulation. These getters are relatively unaffected by air and environmental gases. They can be packaged in a variety of ways to fit particular needs such as porous pellets, fine or coarse powder, or loaded into silicone rubber and molded. The H_2 gettering reactions are extremely irreversible since the H_2 is converted into a solid organic hydrocarbon. These getters are based on the palladium catalyzed hydrogenation of triple bonds to single bonds in aromatic aryl compounds. DEB (1,4 bis(phenyl ethynyl)benzene) mixed with 25% by weight C with 1% Pd, and pressed into a porous pellet is one of the newest and best of these organic hydrogen getters. The hydriding kinetics of this system has been characterized [1–3] using a simple two-volume gas burette system to incrementally titrate getter pellets with H_2 resulting in a series of pressure decay curves, from which the reaction rate (R, 10^{-5} to 10^{-10} mol H (g DEB)$^{-1}$ s^{-1}) was determined as a function of H_2 pressure (P, 100–0.1 Pa), DEB reaction extent (X, 0–21.57 mmol H (g DEB)$^{-1}$), and temperature (T, 273–341 K), and described within a first standard error factor of 1.22 by Eq. (1).

$$\begin{aligned}\text{Rate} = \{&0.010\,e^{-4025/T}P^{(1.84-315/T)}\\ &\times[(5e^{-0.8X}+e^{-0.03X})(1-X/21.57)/6]\}\\ &\{\text{mol H(g DEB pellet)}^{-1}\,\text{s}^{-1}\}\end{aligned} \tag{1}$$

A predecessor to DEB ($X_{\text{MAX}} = 21.57$ mmol H/g, 8 mol H/mol DEB) pellets is diphenyl butadiyne (DPB) pellets, i.e., DEB without the central benzene ring. DPB ($X_{\text{MAX}} = 29.69$ mmol H/g, 8 mol H/mol DPB) has a lower formula weight, a higher specific reaction extent, higher volatility, and forms eutectic mixtures from the reduction products. This paper describes an extension of the DEB experiments to DPB at 17 °C, the extension of the H_2 pressure range to 13 kPa for both, and comparison of the two getter systems.

2. Experimental

The experimental apparatus and number of pellets was the same as that used in the earlier DEB work near ambient temperature [2,3]. A new set of six DPB pellets weighing 126 mg were loaded in the system used for DEB [2,3]. A steel-sheathed, type K thermocouple was located against the glass outer wall of the specimen container of the apparatus and wrapped in several layers of

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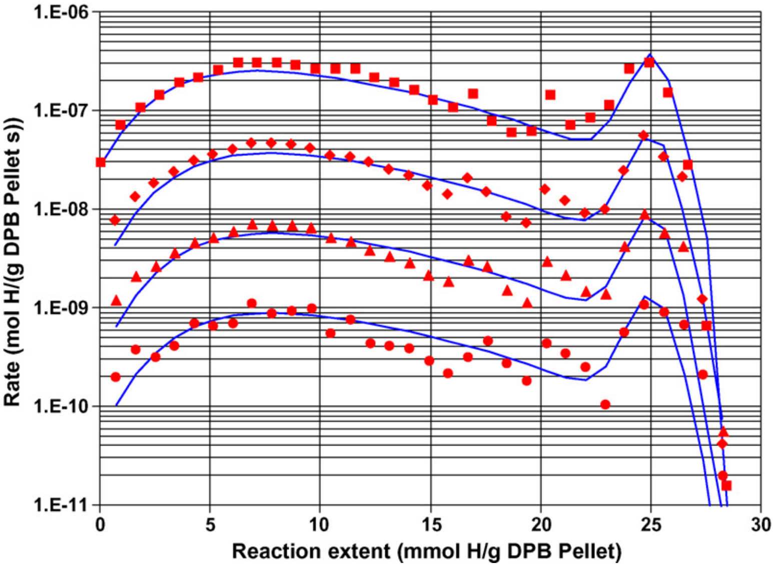

Fig. 1. Hydriding rate isobars (top to bottom 100, 10, 1, and 0.1 Pa) near 17 °C for the 126 mg pellet sample. Solid lines were calculated using Eq. (2).

aluminum foil. Between each experimental run the entire system was evacuated with an ion pump to well below 10 mPa. The ion pump and specimen were isolated, the supply volume (∼1 L) charged to ∼133 Pa with UH_3-filtered H_2, and the valve opened dumping the H_2 onto the specimen. A typical result for an experiment was an apparent exponential decay in H_2 pressure over time to an end-point pressure slightly greater than the initial zero, typically 0.2 Pa; four times greater than that observed for DEB. This quantity of residual gas was too small to qualitatively identify with the available residual gas analyzer. This decay curve was adjusted to 0.00 Pa at the end-point and then fit as the natural logarithm to a fifth-order polynomial (using TableCurve 2D®, SSPS) to accurately represent the data while smoothing the data so that it could be differentiated. This analytical representation of the data also allowed for the data to be thinned from the several thousand data points in an experiment to ∼30 points uniformly spanning the pressure range of the experiment on a logarithmic scale. These calculations were also done for specific values of pressure, so rate isobars could be produced. Thus, from the pressure decay as a function of time, the H_2 pressures, the reaction extent, and the reaction rates were determined parametrically in time. For the DPB pellet data, consumption has a complex kinetic behavior, and the reaction extent dependence was radically different for that of DEB (Eq. (1)) which is a two-stage decay process. The problem was reduced to isobars at 100, 10, 1, and 0.1 Pa and the 100 Pa data was curve fit (TableCurve 2D®, SSPS) for the dependence of the natural logarithm of the rate versus reaction extent. High order polynomials gave a reasonable fit, and the translation of the 100 Pa curve to the lower pressure curves by a simple offset indicated a kinetic order in pressure of ∼0.8 as shown in Fig. 1. Further attempts to utilize the high order polynomial fits indicated that the double precision offered by spread sheets such as Excel® were not adequate to calculate accurate results, so an expression was constructed using simple algebraic forms as shown in Eq. (2) that are less demanding of the parameter precision, similar to the functions used to arrive at Eq. (1).

$$\text{Rate} = P^{0.81}\ \exp[3.147\{(1-\mathrm{e}^{-X/2.93}) - 0.0137X\} + 2.778\mathrm{e}^{-\{(X-25.2)/1.89\}^2} - 21.16\}/(1-X/28.47)^{0.059}]\{\text{mol H(g DPB pellet)}^{-1}\ \text{s}^{-1}\} \tag{2}$$

The terms in the square brackets give the reaction extent dependence of the data. The first term in these brackets gives the early reaction extent pulse shape to the curve in Fig. 1. The second term describes the late reaction extent “pulse” and the last term truncates the rate at stoichiometry value 28.47 as determined by the fit. The solid lines are calculated using the parameters obtained by fitting the entire data set (922 data points) to Eq. (2) (TableCurve 3D® SSPS) yielding the parameters in Eq. (2), and fit shown in Fig. 2. The fit had a first standard error factor of 1.61 mostly due to fitting the reaction extent extremes and other anomalies such as the “ripples” in the rate surface in Fig. 2 between reaction extent 17 and 22 mmol H/g DPB pellets. These “ripples” in the rate surface were

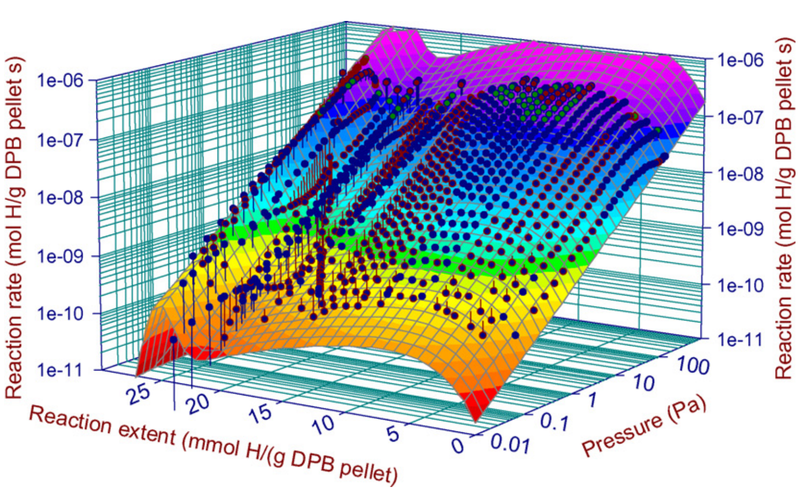

Fig. 2. The hydriding rate of DPB pellets as a function of pressure and reaction extent. Surface is described by Eq. (2).

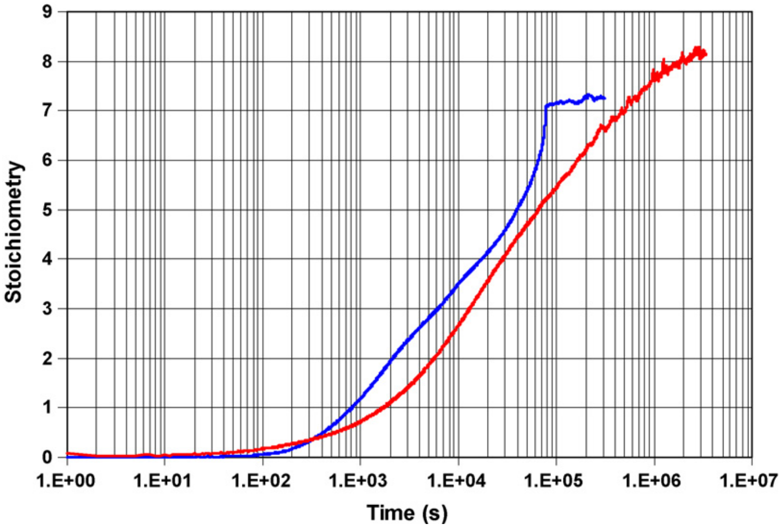

Fig. 3. Hydrogen stoichiometry change in DEB (lower curve) and DPB (upper curve) getter pellets over time for reaction with H_2 at pressures near 10 kPa.

probably due to local regions in the six pellets reaching final stoichiometry (and the increase in rate) before the remainder of the specimen. A 100 Torr pressure gauge (MKS 390AH-00100) was added and these experiments were repeated at initial pressures of ∼13 kPa H_2 for a 126 mg (six pellets) DPB specimen and again for a 120 mg (six pellets) DEB specimen. The results were qualitatively similar to the low-pressure experiments except the reaction went to completion with only an ∼30% pressure drop. The X_{MAX} measured was 22.49 mmol H/g pellets for DEB (104.3% theoretical) achieved after 1 month and 26.60 mmol H/g pellets for DPB (89.6% theoretical) achieved in 1 day. These results are shown as the change in stoichiometry of the getter with time in Fig. 3.

3. Discussion

DPB pellet getters are found to hydride in a very rapid and predictable rate over the pressure range of 134 to <0.1 Pa near 17 °C, with a slow initial rate that increases with reaction extent and remains higher than the initial rate until the reaction terminates before reaching the theoretical maximum reaction extent. In contrast, DEB pellets initially react rapidly, followed by a decaying rate with reaction extent. The higher rate at high reaction extents for DPB is probably due to eutectic formation by the mix of reaction products. This eutectic formation and the associated additional mobility of the remaining reactants is probably responsible for the pulse in the reaction rate at high reaction extents, and may also allow some of the reactants to wick away from the catalyst reducing the total capacity. The visual appearance of a new DPB pellet surface is much more specular (shinier) than that of DEB suggesting that the surface porosity of the DPB pellets may initially be closed. The fully reacted DPB pellets are significantly disfigured by the reaction, whereas the DEB pellets show little change in appearance upon reaction.

Acknowledgements

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