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TG/DTA of hydrogen reduction kinetics of TiO_2 supported PdO chemochromic pigments

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ABSTRACT

Titania supported palladium oxide (PdO) chemochromic pigments have been used in various hydrogen sensing devices as a passive technique for detecting hydrogen leaks. Here, we present new data for the kinetics of titania-supported PdO reduction by hydrogen gas by means of thermogravimetric/differential thermal (TG/DTA) analysis. The TG/DTA thermograms show a two step process. The first step in the process is an induction period during which no color change occurs – having zero reaction order with respect to palladium oxide concentration [PdO]. A color change is associated with the second step during which the adsorbed hydrogen reacts with PdO···H species to form water. This step has fast kinetics with reaction order of 0.55 and zero with respect to [PdO···H] and [H_2], respectively.

1. Introduction

Ability to detect leaks at the hydrogen storage, transmission and usage sites is crucial for its safe handling and use. Hydrogen has high diffusivity that makes it prone to leakage from joints and pipe flanges. Since many hydrogen applications require high purity gas and will not tolerate any additives to the gas, it is of interest to develop methods and materials capable of pinpoint detection of the hydrogen leak location when it occurs. Presently, most hydrogen detection research has been focused on the development of electronic sensors. Electronic sensors have several drawbacks including loss of sensitivity in the field due to environmental effects and costs, among others. An alternative to active H_2 sensors is passive (i.e. chemochromic) detection of hydrogen using a special silicone matrix that contains titania (TiO_2) supported palladium oxide (PdO) pigments [1–4]. The color change occurs as a result of PdO reduction by hydrogen to form elemental Pd.

In this paper, we present and discuss the kinetic data obtained for hydrogen reduction of PdO/TiO_2 pigments over the temperature range of 80–120 °C.

2. Experimental

2.1. Materials

Titania (mainly, rutile crystalline form) with an average particle size of 1 μm was obtained from Aldrich. HCl, NaOH, and $PdCl_2$ were acquired from Acros.

2.2. Pigment preparation

Using a modified procedure reported by Sakamoto et al. [5], several chemochromic pigments with 1.5 wt%, 3 wt% and 6 wt% Pd content were synthesized. For example, pigments having 3 wt% Pd were prepared by dissolving 1.0 g of $PdCl_2$ in 50 mL of 2 M hydrochloric acid (HCl) solution. Two syringes were filled, one with 30 mL of $PdCl_2$ solution and the other with 30 mL of 2 M NaOH solution. Both syringes were placed in a programmable syringe pump, and the injection rate was set to 0.5 mL/min. Then, 25 mL of each solution was added to a TiO_2 slurry (10 g TiO_2 in 100 mL H_2O) heated to 70 °C at a pH of 10. During this preparation activity, solution pH remained within the 10–11 (±0.5%) range. The pH was then adjusted to 8 by adding 3 M HCl solution. The pulp was stirred for an hour and then filtered, washed, and oven dried at 110 °C. Eqs. (1)–(2) show the chemical transformation of $PdCl_2$ to PdO:

$$PdCl_2 + 2NaOH \rightarrow Pd(OH)_2 + 2NaCl \quad (1)$$

$$Pd(OH)_2 \xrightarrow{\Delta} PdO - H_2O \quad (2)$$

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2.3. Thermogravimetric/differential thermal analysis (TG/DTA)

Thermogravimetric/differential thermal analysis (TGA) were carried out by loading between 7 and 10 mg of each pigment sample into a platinum sample pan loaded into a Perkin-Elmer Diamond TG/DTA with a ±0.2 μg and ±0.06 μV sensitivity for TG and DTA, respectively.

Typical PdO/TiO_2 pigment was placed inside the sample holder and the instrument was purged with helium for 5 min at a set temperature (30, 80, 100, and 120 °C). Then the helium sweep gas was switched to another having desired hydrogen concentration – that is 2% H_2 in argon, 10% H_2 in argon, and 50% H_2 in argon. The TG/DTA thermograms presented in this article only show the portion of the data for which the carrier gas had been switched to hydrogen, during which reduction of PdO to Pd occurred. The ultra high purity (99.999%) H_2/Ar mixed gas cylinders with varying hydrogen concentration were used as received.

3. Results and discussions

Previously we had reported that TiO_2/PdO membranes (pigments encapsulated in silicone matrix and drawn as membranes), when in contact with hydrogen, do not change color immediately and there is an induction period before discoloration begins [4]. In order to better understand this phenomenon, pigments were analyzed with TG/DTA instrument by executing a series of carefully designed experiments.

3.1. TG/DTA analysis of a typical chemochromic TiO_2/PdO pigment

Fig. 1 depicts the thermogram of PdO reduction to Pd in a 2% H_2/Ar atmosphere at 30 °C temperature. The thermogram can be divided into three steps. During the first step, a small but discernible weight gain is seen. This initial weight gain is followed by a rapid weight loss which occurs as a result of an exothermic reaction (second step). A slow weight gain that extends well past the exothermic event is characteristic of the third step. This experiment was repeated several times and results were reproducible.

Furthermore, a series of experiments were conducted during which the pigments were visually monitored as they passed through the first, second, and third periods. This was done by stopping the run at different time intervals and removing the sample for visual inspection. For each step, a fresh sample was loaded into the TG/DTA instrument. We were able to confirm that no color change occurred during the first step (initial 5 min period during which the sample weight increases) and by the end of the second, exothermic period that lasts about 3 min, the color of the sample had completely changed. During the third period, the color appeared unchanged.

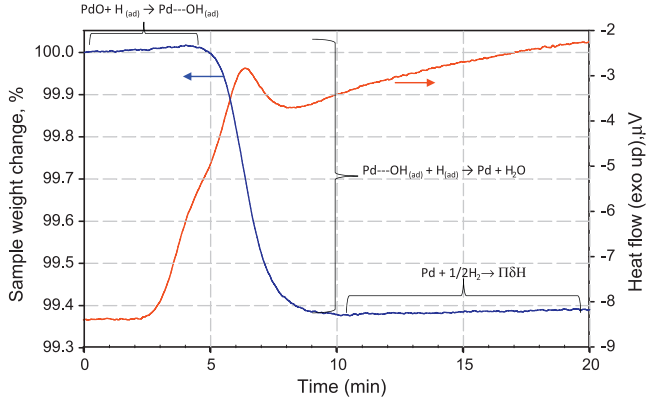

Fig. 1. TG/DTA thermogram depicting TiO_2/PdO pigment (having 3 wt% Pd loading), isothermal run at 30 °C and sweep gas: 2% H_2 in argon.

Investigation of PdO reduction by hydrogen has been reported in literature [6–9]. Following reactions leading to the formation of water have been postulated:

$$H_2(g) \leftrightarrow 2H(ad) \quad (3)$$

$$PdO + H(ad) \leftrightarrow PdO\cdots H(ad) \quad (4)$$

$$PdO\cdots H(ad) + H(ad) \xrightarrow{K} Pd + H_2O \quad (5)$$

Reaction between adsorbed hydrogen and PdO (Eq. (4)) is thought to be the rate-limiting step which is followed by a rapid reaction between adsorbed H and OH to form water (Eq. (5)).

An induction period during PdO reduction with CH_4 has been reported by Su et al. [6] who shown that its duration was longer for PdO reduction by H_2 gas. These researchers suggested a nucleation-controlled reduction of PdO by CH_4 and a shell wise reduction by H_2.

Hence, the first weight gain in TG thermogram appears to be associated with this induction period, i.e. Eq. (4), which is the rate-limiting step. Eq. (5) denotes the exothermic step of hydrogen adsorption on PdO···H species, which is also the pigment discoloration reaction.

The heat of adsorption of H_2 on Pd surface is 0.5 eV while the heat of solution of H_2 in Pd is 0.1 eV [9]. This means that Pd can easily take up hydrogen. In other word, adsorbed hydrogen on the surface becomes dissolved in Pd forming a hydride as follows:

$$Pd + \tfrac{1}{2}H_2 \rightarrow PdH \quad (6)$$

This phenomenon explains the slight weight increase during the third period of Fig. 1. Furthermore, it is known that hydrogen solubility in Pd increases as the temperatures decrease.

Fig. 2 depicts the weight change associated with the reduction of TiO_2/PdO pigment in the presence of 10 vol% H_2 in argon at 100 °C. Although the measured values of weight change are consistently higher for all three samples examined, compared to the predicted values (see Table 1), nonetheless, the trend is consistent with the amount of Pd loading of the TiO_2/PdO samples.

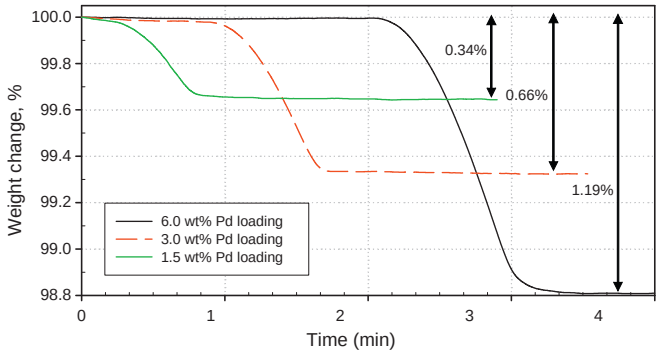

Fig. 2. TGA data for TiO_2/PdO (1.5, 3, 6 wt% Pd loading) weight change at 100 °C and in the presence of 10 vol% hydrogen in argon.

Table 1
Predicted vs. measured weight change due to the reduction of PdO by hydrogen ($PdO + H_2 \rightarrow Pd + H_2O$).

Pd loading in TiO_2/PdO, wt%	Predicted weight change, %	Measured weight change, %	Ratio of weight changes predicted/measured
1.5	0.23	0.34	0.68
3	0.45	0.66	0.68
6	0.90	1.19	0.76

A close examination of the data presented in Fig. 2 reveals that the initial step at the onset of reduction is the rate limiting step. TiO_2/PdO pigments with lower Pd loading seem to undergo color change (second step) sooner, i.e. with shorter induction times. For example, the induction time for discoloration of the pigment having 1.5 wt% Pd loading was 0.2 min while for those with 3 and 6 wt% Pd loading, the induction times observed were more than 1 min and approximately 2 min, respectively. The increase in induction time was found to be linear with the amount of Pd loading and therefore the zero order kinetics for this step was confirmed.

3.2. Kinetics of hydrogen induced color change

Since kinetic data provide information about the rate-limiting step only, in theory, post-reduction (discoloration) processes should neither affect the overall rate nor appear in the overall rate equation. However, complete understanding of the process still requires a systematic examination of the entire event – from the moment membrane is exposed to H_2 till its complete discoloration.

The rate of hydrogen adsorption on PdO···H species (υ_o) in Eq. (5), i.e. discoloration step, for pigments presented in Fig. 2 was determined as the slope of best fitted line. The rate law for the this reaction is expressed as Eq. (7) and by using excess amounts of hydrogen the equation can be rewritten as Eq. (8) when $k' = k[H_{(ad)}]^b$. [PdO···H] has a direct relationship with [Pd] and therefore, by plotting the reaction rates against [Pd] in a logarithmic scale the reaction order (a) can be found. This plot is presented in Fig. 3 and the slope, i.e. reaction order (a) was found to be 0.55.

$$\upsilon_o = k[\mathrm{PdO}\cdots\mathrm{H}]^a[\mathrm{H}_{(ad)}]^b \quad (7)$$

$$\upsilon_o = k'[\mathrm{PdO}\cdots\mathrm{H}]^a \quad (8)$$

Fig. 4 depicts the extent of weight change associated with the loss of oxygen (as a result of PdO reduction) during discoloration at 100 °C, for 2%, 10%, and 50 vol% H_2 in argon and the pigment Pd loading of 3 wt%. Again, by plotting (υ_o) (Table 2) against H_2 gas concentration (Fig. 5), the reaction order (b) with respect to H_2 was calculated to be zero – within the margin of error.

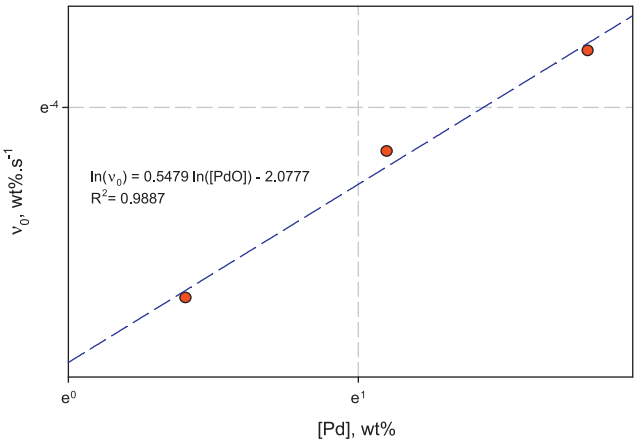

Fig. 3. Rate of hydrogen adsorption on PdO···H species at 100 °C vs. Pd loadings of 1.5, 3 and 6 wt%. Reaction order with respect to [PdO···H] = 0.55.

Table 2
Hydrogen adsorption rates on PdO···H species, at 100 °C and 3 wt% Pd loading, using 2, 10, and 50 vol% of hydrogen in argon.

$P_{[H2]}$, atm ([H_2], vol%)	υ_o (wt% s^{-1})
0.02 (2)	1.05e-03
0.1 (10)	9.97e-04
0.5 (50)	9.60 e-04

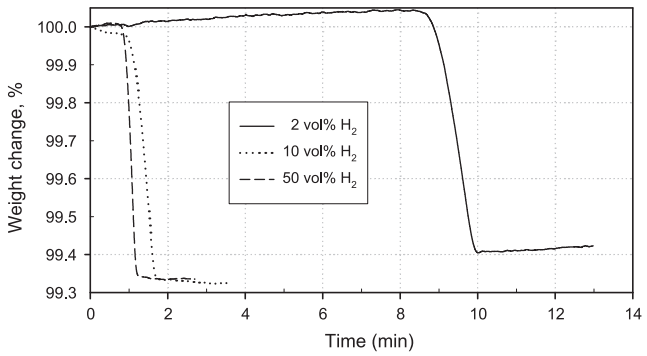

Fig. 4. TGA thermogram of TiO_2/PdO pigments (3% Pd loading) at 100 °C and in the presence of 2%, 10%, and 50% by volume hydrogen in argon.

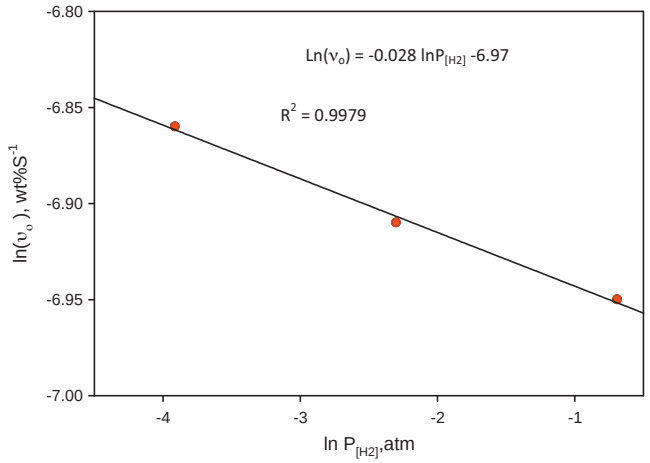

Fig. 5. Rate of hydrogen adsorption on PdO···H species at 100 °C for chemochromic pigments having 3 wt% Pd exposed to 2, 10, and 50 vol% H_2 in argon, reaction order with respect to hydrogen ~0.

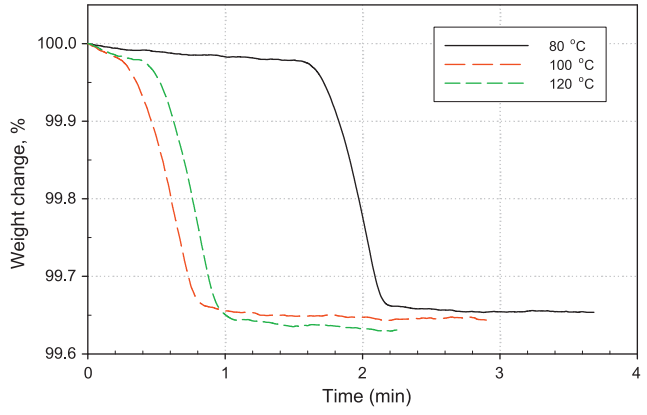

Fig. 6. TGA thermogram of TiO_2/PdO pigments having 1.5 wt% Pd loading at 80 °C, 100 °C and 120 °C, and exposed to 10 vol% hydrogen in argon.

Fig. 6 depicts a TGA thermogram showing the effect of temperature on the rate of PdO reduction by hydrogen. The data suggest that varying reaction temperature (with the temperature range of 80–120 °C) has no appreciable effect on the rate of reaction associated with Eq. (5), i.e. discoloration step. An increase in reaction rate is observed when the temperature is increased from 80 to 100 °C but further increase to 120 °C causes a deceleration. Higher hydrogen concentrations have shown to shorten the time for the first step, i.e. rate limiting step.

4. Conclusions

The reduction of PdO/TiO_2 chemochromic pigments by hydrogen proceeds through two stages. First, hydrogen is dissociatively adsorbed on the surface of the PdO particles forming [PdO···H] intermediate. This step is associated with an induction period during which no color change occurs and appears to be the rate limiting step. This induction period occurs as a zero order event with respect to [PdO] and can be shortened by using higher concentration of hydrogen or elevated temperatures. Second step involves a fast reaction between adsorbed hydrogen and hydroxyl radicals on the palladium surface forming water. Color change occurs during this step and data indicate that it is a reaction of 0.55 and zero order with respect to [PdO···H] and $[H_2]$ concentrations, respectively. Varying temperature has no appreciable effect on the rate of hydrogen adsorption on PdO···H species, i.e. discoloration step.

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References

[1] J.E. Captain, B.V. Peterson, M.C. Whitten, S. Trigwell, C.M. Berger, N. Mohajeri, G. Bokerman, N.Z. Muradov, A. T-Raissi, Chemochromic hydrogen detection, in: Proceedings of SPIE Conference, Orlando, Florida, 17–21 April, 2006.
[2] N. Mohajeri, A. T-Raissi, G. Bokerman, J.E. Captain, B.V. Peterson, M.C. Whitten, S. Trigwell, C.M. Berger, Effects of PdO distributions over TiO_2 particles on its chemochromic behavior for hydrogen detection, in: TMS 2007 Annual Meeting, Orlando, Florida, February 25–March 1, 2007.
[3] G. Bokerman, N. Mohajeri, N.Z. Muradov, A. T-Raissi, Gas permeable chemochromic compositions for hydrogen sensing, U.S. Pat. App. No. 11/414,900, 2006.
[4] N. Mohajeri, A. T-Raissi, G. Bokerman, J.E. Captain, B.V. Peterson, M. Whitten, S. Trigwell, C. Berger, J. Brenner, TEM-XRD analysis of PdO particles on TiO_2 support for chemochromic detection of hydrogen, Sens. Actuators B: Chem. 144 (2010) 208–214.
[5] M. Sakamoto, H. Okuda, H. Futamata, Pigments for sensing gas leakage and process for producing the same, U.S. Pat. No. 5,849,073.
[6] S.C. Su, J.N. Carstens, A.T. Bell, A study of the dynamics of Pd oxidation and PdO reduction by H_2 and CH_4, J. Catal. 176 (1998) 125–135, and references therein.
[7] T. Engel, H. Kuipers, A molecular-beam investigation of the reaction $H_2 + ½O_2 \rightarrow H_2O$ and Pd(1 1 1), Surf. Sci. 90 (1979) 181–196.
[8] C. Nyberg, C.G. Tengstål, Vibrational excitation of hydrogen and oxygen on Pd(1 0 0), Surf. Sci. 126 (1983) 163–169.
[9] P.L. Levine, K.E. Weale, Palladium + hydrogen equilibrium at high pressures and temperatures, Trans. Faraday Soc. 56 (1960) 357–362.