HT Combinatorial Screening of Novel Materials for High Capacity Hydrogen Storage

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This presentation does not contain any proprietary or confidential information
Objectives

- Develop (*i.e.* design, build, test and verify) a high throughput screening device based on FSEC-developed H$_2$ sensing materials applicable to a broad range of adsorbents, including MOFs, various doped & undoped hydrides so that methods for increasing H$_2$ adsorption energies beyond 5 kJ/mol can be identified.

- Develop a rapid screening method & demonstrate the ability to reproducibly screen 10/100 hydrogen sorbing materials per run.

- Measure the amount of H$_2$ released for up to 10/100 solid adsorbents, simultaneously, from SA/LN2 to 423 K (150$^\circ$C) and pressures from 10 torr to 50 bars.
FSEC’s Chemochromic $H_2$
Sensing Materials & Applications

- Industries producing or consuming $H_2$ (e.g. refineries) & others (e.g. NASA).

- Hydrogen Economy
  - Transportation
  - Storage
  - Fuel Cells

Courtesy of NASA-KSC
Accomplishments

At FSEC, we have:

- Formulated, prepared & characterized many novel chemochromic materials for the visual detection of hydrogen gas.
- Developed a technique for the implementation of PdO-based & other “smart pigments”.
  

- Synthesized novel chemochromic materials based on POM complexes and others.
• Change color at temperatures as low as -40°C
• Employ gas permeable matrices for the pigment encapsulation that make them selective toward hydrogen detection
• Has been fielded by NASA.
Synthesis of TiO$_2$/PdO Based Pigments

**Reaction Equation:**

$\text{TiO}_2 + \text{H}_2\text{O}\rightarrow \text{PdCl}_2 + \text{H}_2\text{O} + \text{HCl}$

**TiO$_2$ Sample**

<table>
<thead>
<tr>
<th>TiO$_2$ Sample</th>
<th>Degussa P-25</th>
<th>Aldrich</th>
<th>Fisher</th>
<th>DuPont R103</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size ($\mu$m)</td>
<td>0.02-0.04</td>
<td>0.5</td>
<td>0.1-0.5</td>
<td>0.05-0.2</td>
</tr>
</tbody>
</table>
A 25-mil thick section of chemochromic film after exposure to various quantities of hydrogen gas.
PdO on Degussa P-25 TiO$_2$
Quantifying Color Change

Parameters affecting the appearance of color are:

- **Basic pigment formulation**
- **Surface characteristics** (gloss, texture, pattern, etc.)

0/45- or 45/0-degree instruments are most often used as they avoid the specular component, like a person does when examining the appearance of color.
Quantifying Color Change
(cont’d)

❖ Using ColorTec-PCM colorimeter

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

L*- Lightness Value
a*- position on red-green axis
b*- position on yellow-blue axis

❖ Greater the $\Delta E^*$ value, higher the color contrast
Quantifying Color Change
(cont'd)
Quantifying Color Change

Fastest color change

ΔE vs. H₂ Exposure Time for Various TiO₂ Supports

Data courtesy of NASA-KSC & Arctic Slope Research Corp.
TEM of PdO on Degussa P-25 TiO₂

- Well dispersed PdO particles
- Strongly attached to TiO₂ support
- Homogenous
- Particle size ~2.5 nm
TEM of PdO on DuPont

R103 TiO$_2$

- Well dispersed spherical PdO particles
- Loosely attached to TiO$_2$ support
- Non-homogenous
- Particle size > 5 nm
FSEC's New & Proprietary
$H_2$ Sensing Pigment

$H_2$ FLOW

$H_2$ SENSING PIGMENT & SUPPORT
Several formulations developed at FSEC can be used in “repeated coloration/discoloration” applications including HT screening of hydrogen storage materials as the following video shows.
Single Cell Design of FSEC’s HT Combinatorial Screening Apparatus

SS304 SPECIMEN CHAMBER - OUTSIDE

KALREZ O-RING & SCREW FOR 600F, 5 atm

H2 IN

VACUUM PUMP

TO

H2 OUT

TC

SPECIMEN

THERMALLY CONDUCTIVE EPOXY

CARTIDGE HEATER 100W

GAURD HEATER 30W

LN2 COOLING COIL

He SWEEP GAS IN

H2 OUT

H2 IN

SS304 SPECIMEN CHAMBER - INSIDE

SS304 SPECIMEN CHAMBER - INSIDE
A large number of hydrogen sensing pigments suitable for HT H₂ storage materials screening have been synthesized using PdO on TiO₂ supports and other compounds.

The extent of color change has been determined as a function of time and amount of H₂ within the membranes.

PdO on Degussa P-25 with smallest TiO₂ particles shows fastest discoloration and highest color contrast.

A HT combinatorial screening apparatus has been designed for testing up to 100 individual samples, in few minutes, at temperatures & pressures in the range of LN2-150°C and 10-38 ktorrs, respectively.
Acknowledgment

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