Study and development of localised surface plasmon resonance based sensors using anisotropic spectroscopy

Presented by Mr. William L. Watkins
Supervised by Dr. Yves Borensztein

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Jury members

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Président

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Rapporteur

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Maître de conferences
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Examineur

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Ecole doctorale : Physique et chimie des matériaux – ED397
Laboratoire : Institut des nanosciences de Paris
Equipe : Physico-chimie et dynamique des surfaces
“Hydrogen economy”, energy of the future?
Need for $\text{H}_2$ sensors

- Highly explosive in air

<table>
<thead>
<tr>
<th>Pure air</th>
<th>Explosive range</th>
<th>Pure $\text{H}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4%</td>
<td></td>
<td>70%</td>
</tr>
</tbody>
</table>

Solution

Development of **optical** sensing

Formation of Palladium hydride

$H_2 (g) + 2Pd \rightarrow 2PdH$

- Best optical sensitivity
  - 0.1% in $N_2$
  - 0.5% in air

Use anisotropic **plasmon** as an **optical method** for **high sensitivity sensing**

- Surface interaction of $\text{H}_2$ with Au NP
- $\text{H}_2$ sensing with Pd
1. LSPR fundamentals
   - LSPR for sensing
   - Anisotropy in LSPR
   - Anisotropy spectroscopy

2. Fabrication of anisotropic samples
   - Fabrication of Au samples
   - Model the spectra
   - Optimising the anisotropy

3. Fundamental study: surface interaction of $\text{H}_2$ with Au
   - Experimental insight into the mechanism
   - Determination of the charge transferred

4. Application study: sensing of $\text{H}_2$ with LSPR
   - Need for better optical sensing
   - Use of Au and Pd sensors
   - Use of pure Pd
   - Increase in sensitivity
Properties of metals at the nanoscale

Localised surface plasmon resonance (LSPR)

**Definition:** collective oscillation of conduction electron excited by an oscillating electric field

Absorption in the case of Au in the Visible

\[ \sigma_{abs} \propto \text{Im} (\alpha) \]

\[ \alpha_{sphere} = 3V \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \]
LSPR shift: Change in the medium

\[ \alpha_{sphere} = 3V \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \]

Increase in \( \varepsilon_m \) leads to red shift

LSPR used as sensors
\[ \alpha_{sphere} = 3V \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \]

\[ \Delta \lambda \]

\[ \sigma_{abs} [\text{a.u.}] \]

\[ \text{Wavelength [nm]} \]

\[ \varepsilon(\omega) = 1 - \frac{\Omega_p^2}{\omega(\omega + i\tau^{-1})} + \varepsilon^{ib}(\omega) \]

\[ \Omega_p = \left( \frac{Ne^2}{\varepsilon_0 m} \right)^{1/2} \]

\[ \frac{1}{2} \frac{\Delta N}{N} \approx -\frac{\Delta \lambda_{LSPR}}{\lambda_{LSPR}} \]

LSPR shift: Charge transfers

Adsorbed entities

Material \( \varepsilon \)

Drude model

Decreases in \( N \) leads to red shift

LSPR used surface reactivity study
Measuring the shift: conventional technique

**Technique**: UV-Vis spectroscopy

- **Spectral measurement**
- **Curve fitting** (ex: Gaussian fit)

**Issues**

**Absolute**
- Sensitive to fluctuations: light, pollution, vibration
- Needs reference

**Spectral**
- Requires monochromator
- Needs fitting of the curve

**Monochromator**
- Compromise: resolution & bulkiness

Use of anisotropy to solve these issues
# Anisotropy in LSPR

**MICROscopy anisotropy**

\[
\alpha_{sphere} = 3V \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}
\]

\[
\alpha_{ellip.} = V \frac{\varepsilon - \varepsilon_m}{\varepsilon_m + L (\varepsilon - \varepsilon_m)}
\]

Depolarisation Factor

- Ellipsoid
- Two maxima for the two orthogonal polarisations

**MACROscopy anisotropy**

- Does not have to be perfect
- Needs to be **globally anisotropic**

---

*A micrograph showing an ellipsoid with two maxima for the two orthogonal polarisations.*
Use of Transmittance anisotropy spectroscopy

Solution: Anisotropic spectroscopy

- RAS (Aspnes)
- TAS

Technique known and used at INSP
For anisotropic metal

\[
\frac{\Delta R}{R} \text{ or } \frac{\Delta T}{T} = \frac{T_A - T_B}{T}
\]


MACROscopy anisotropy

Does not have to be perfect

Needs to be globally anisotropic

Absolute

\[\Delta \sigma \left\frac{\sigma_{obs}}{\sigma}\right\]

Differential
Use of Transmittance anisotropy spectroscopy

- Shift influences both peaks
- TAS shifts as well
Use of Transmittance anisotropy spectroscopy

- Shift influences both peaks
- TAS shifts as well
- Can now work at **single wavelength**
  - The **steeper** the **better**
Use of Transmittance anisotropy spectroscopy

**Issues**

**Absolute**
- Sensitive to fluctuations: light, pollution, vibration
- Needs reference

**Spectral**
- Requires monochromator
- Needs fitting of the curve

**Monochromator**
- Compromise: resolution & bulkiness

**Relative & differential**
- Better reproducibility
- Signal more stable
- Better sensitivity
- No need for monochromator nor fitting

The steeper the better

\[
\frac{\Delta \sigma}{\sigma} \quad \Delta \lambda
\]
1. **LSPR fundamentals**
   - LSPR for sensing
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   - Fabrication of Au samples
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4. **Application study**: sensing of H₂ with LSPR
   - Need for better optical sensing
   - Use of Au and Pd sensors
   - Use of pure Pd
   - Increase in sensitivity
Our requirements: scalability in mind

- **Simple** to synthesise
- Use **non-expensive** materials
- **Large** surface **area** samples (mm²)
- **Small** metallic **nanoparticles** (⌀≈ 10nm)
- Global **anisotropy** of the sample
- **Exposed** nanoparticles
**Known methods**

<table>
<thead>
<tr>
<th>Lithography</th>
<th>Chemical synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>✗ Simple</td>
<td>✓ Simple</td>
</tr>
<tr>
<td>✗ Non-expensive</td>
<td>✓ Non-expensive</td>
</tr>
<tr>
<td>✗ Large area</td>
<td>✓ Large area</td>
</tr>
<tr>
<td>✗ Small NPs</td>
<td>✓ Small NPs</td>
</tr>
<tr>
<td>✓ Anisotropic</td>
<td>✗ Anisotropic</td>
</tr>
<tr>
<td>✓ Exposed</td>
<td>✗ Exposed</td>
</tr>
</tbody>
</table>


**Known methods**

<table>
<thead>
<tr>
<th>Oblique Angle Deposition on stepped surfaces</th>
</tr>
</thead>
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<tr>
<td>- Simple</td>
</tr>
<tr>
<td>- Non-expensive</td>
</tr>
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<td>- Exposed</td>
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</table>


<table>
<thead>
<tr>
<th>Method that inspired the thesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Applying this to simpler substrates</td>
</tr>
</tbody>
</table>

Known methods: choice of OAD

- Simple
- Non-expensive
- Large area
  - Small NPs
  - Anisotropic
  - Exposed

Evaporation at grazing angle
Known methods: choice of OAD

- Simple
- Non-expensive
- Large area
- Small NPs
- Anisotropic
- Exposed

Evaporation at grazing angle

Weak structural anisotropy

Anisotropic spectrum
Calculated with supported ellipsoids

\[ \alpha_{\text{ellip.}} = V \frac{\varepsilon - \varepsilon_m}{\varepsilon_m + L (\varepsilon - \varepsilon_m)} \]

- \( a_1 = 3.6 \text{ nm} \)
- \( a_2 = 4.7 \text{ nm} \)
- \( a_3 = 1.2 \text{ nm} \)
- \( K = 16 \text{nm} \)

Model reproduces experiments

Optimising the anisotropy

- Working wavelength from **600nm to 800nm**
- The **thickness** controls the anisotropy (slope)
- The **angle** controls the resonance wavelength

Evaporation **parameters** controls the **shape** of the anisotropy
1. **LSPR fundamentals**
   - LSPR for sensing
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3. **Fundamental study : surface interaction of H\textsubscript{2} with Au**
   - Experimental insight into the mechanism
   - Determination of the charge transferred

4. **Application study : sensing of H\textsubscript{2} with LSPR**
   - Need for better optical sensing
   - Use of Au and Pd sensors
   - Use of pure Pd
   - Increase in sensitivity
**What is and isn’t known in the lit.?**

**Knowns**

- **H₂** molecules adsorb and dissociate on the edges on the Au NPs


- **Charge transfer** from bulk to bond

  \[
  \frac{1}{2} \frac{\Delta N}{N} \approx \frac{\Delta \lambda_{lsp}}{\lambda_{lsp}}
  \]

  N decreases then **red shift**


**Unknowns**

- What is the **becoming** of the **H** after adsorption?

- What is the **charge transfer**?
What is and isn’t known in the lit.?

Reminder

$H_2 / Ar$ cycles on Au NP

Red shift

What is and isn’t known in the lit.?

H₂ / Ar cycles on Au NP different size

Red shift

Hypothesis: \( \Delta N \propto \text{diameter} \)

What is and isn’t known in the lit.? 

Hypothesis: \[ \Delta N \propto \text{diameter} \]

\[ \Delta N \propto \text{surface area} \]

The surfaces play a role in the reaction mechanism.
Adsorption on the (100) or (111) ?

DFT calculations

\[
E_{H-H(g)} = 0 \text{ eV}
\]
\[
kT = 0.03 \text{ eV} \at T = 298 K
\]

\[
H - \text{Au}_{(100)} = -0.01 \pm 0.02 \text{eV}
\]

Most stable surface

\[
H - \text{Au}_{(111)} = +0.10 \pm 0.02 \text{eV}
\]

New mechanism acknowledging the surface

\[ H - \text{Au}_{(100)} = -0.01 \pm 0.02\text{eV} \]

Most stable surface

Proposed mechanism

1. Adsorption on the edges
2. Dissociation & desorption on the edges
3. Diffusion on the (100) facets
4. Desorption from the facets

**New mechanism** acknowledging the surface

\[
H - \text{Au}_{(100)} = -0.01 \pm 0.02eV
\]

**Proposed mechanism**

1. Adsorption on the edges
2. Dissociation & desorption on the edges
3. Diffusion on the (100) facets
4. Desorption from the facets

**Kinetic analysis: determination of the coverage in H**

**Measure the coverage $\theta$ in H**

<table>
<thead>
<tr>
<th>Proposed mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Adsorption on the edges</td>
</tr>
<tr>
<td>2 Dissociation &amp; desorption on the edges</td>
</tr>
<tr>
<td>3 Diffusion on the (100) facets</td>
</tr>
<tr>
<td>4 Desorption from the facets</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\theta_{edge}$: edge coverage</th>
<th>$\theta_{(100)}$: surface coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>➢ Adsorption on the edges $r_a(\theta_{edge}) = k_a(T) (1 - \theta_{edge})^2 \phi$</td>
<td></td>
</tr>
<tr>
<td>➢ Desorption from the edges $r'<em>d(\theta</em>{edge}) = k'<em>d(T) \theta</em>{edge}^2$</td>
<td></td>
</tr>
<tr>
<td>➢ Migration from the edges $\rightarrow$ facets $r_{mig}(\theta_{edge}, \theta_{(100)})$</td>
<td></td>
</tr>
<tr>
<td>➢ Migration from the facets $\rightarrow$ edges $r'<em>{mig}(\theta</em>{(100)}, \theta_{edge})$</td>
<td></td>
</tr>
<tr>
<td>➢ Desorption from the facets $r_d(\theta_{(100)}) = k_d(T) \theta_{(100)}^2$</td>
<td></td>
</tr>
</tbody>
</table>

\[
\frac{d\theta_{edge}}{dt} = r_d(\theta_{(100)}) - r'_d(\theta_{edge}) - r_{mig}(\theta_{edge}, \theta_{(100)}) + r'_{mig}(\theta_{(100)}, \theta_{edge}) = 0
\]

\[
\frac{d\theta_{(100)}}{dt} = r_{mig}(\theta_{edge}, \theta_{(100)}) - r'_{mig}(\theta_{(100)}, \theta_{edge}) - r_d(\theta_{(100)}) = 0
\]


\[
A\theta_{(100)} = \frac{F^{1/2}}{F^{1/2} + \left(1 + \frac{k_d}{A^2 k'_d}\right)^{1/2}}
\]

$A$ is the active area, $k_d$ is the desorption rate coefficient, $k'_d$ is the migration rate coefficient.

$F$: flow of $H_2$ (g) $F \propto p(H_2)$

Parameter to fit

31
Kinetic study: measure the coverage in H

\[ A\theta_{(100)} = \frac{F^{1/2}}{F^{1/2} + \left(1 + \frac{k_d}{A^2k_d'}\right)^{1/2}} \]

Parameter to fit

Determination of the H coverage \( \theta_{(100)} \)

We need to know the **number** of adsorbed **H atoms**

Charge transfer per H atoms

---

Estimation of the charge transfer

Equilibrium shape


How many Au atoms?

Surface area (100)

50 \( \text{nm}^2 \) ⇔ 600 Au atoms

Volume

400 \( \text{nm}^3 \) ⇔ 24 000 Au atoms

Charge transferred per H-Au bond

\[ \delta^- \approx -0.2 \text{ e per bond} \]

\[ \frac{1}{2} \frac{\Delta N}{N} \approx \frac{-\Delta \lambda_{\text{LSPR}}}{\lambda_{\text{LSPR}}} \]

\[ \frac{\Delta N}{N} = -1.5 \cdot 10^{-3} \]

\[ -35 \text{ e}^- / \text{NP} \]

\[ \theta = 16\% \]

96 H on Au(100)

### What did others find?

<table>
<thead>
<tr>
<th>Ref.</th>
<th>System</th>
<th>Charge transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>X.-J. Kuang, et al. (2013)</td>
<td>$Au_{13}$</td>
<td>$-0.1 , e$</td>
</tr>
<tr>
<td>A. Lyalin et al. (2011)</td>
<td>$Au_{20}$</td>
<td>No CT</td>
</tr>
<tr>
<td>Faraday Discussions, 152, 0, 26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S. Zhao, et al. (2010)</td>
<td>$Au_{5}$</td>
<td>$+0.3 , e$</td>
</tr>
<tr>
<td>J. Phys. Chem. A, 114, 14, 4917–4923</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F. Libisch et al. (2013)</td>
<td>$Au_{12}$</td>
<td>$-0.8 , e$</td>
</tr>
<tr>
<td>Zeitschrift für Physikalische Chemie, 227.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hu, M., et al. (2013)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Confirmed by DFT calculation**

**Negative charge transfer** from the NP to the H-Au bond
What is the becoming of the H after adsorption?

Insight into the mechanism of H₂ adsorption on Au

Surfaces play a role

What is the charge transfer?

First quantitative experimental results

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   - Need for better optical sensing
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   - Use of pure Pd
   - Increase in sensitivity
Reactivity of Pd with hydrogen

Formation of Palladium hydride

\[ H_2(g) + 2Pd \rightarrow 2PdH \]

- \( p(H_2) \gg 1\% \Rightarrow \beta \)
- \( p(H_2) \approx 1\% \Rightarrow \alpha + \beta \)
- \( p(H_2) \ll 1\% \Rightarrow \alpha \)

Need to detection the \( \alpha \) phase i.e. \( p(H_2) \ll 1\% \)

Can Pd be used alone?

LSPR in the near IR


Qualitatif comparison with Au

Pd LSPR

Extinction [%] vs. Wavelength [nm]

Abs [a.u.] vs. Wavelength [nm]

Very large
Can Pd be used alone?

Pd LSPR

LSPR in the near IR


Tiny effect in the α-phase

Not ideal for high sensitivity sensing

How are LSPR sensors made for $\text{H}_2$ detection?

Use Pd to absorb $\text{H}_2$ and shift the LSPR of Au NPs.
How are LSPR sensors made for $\text{H}_2$ detection?

- Evaporation of (0.2nm) Pd on Au

Atmospheric Pressure (1 atm)

Room temperature (20°C)

More sensitive with Pd on Au

Error gas $p(\text{H}_2) \approx 10\%$

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>63%</td>
<td>16%</td>
</tr>
<tr>
<td>4%</td>
<td>1%</td>
</tr>
<tr>
<td>0.25%</td>
<td>0.06%</td>
</tr>
<tr>
<td>0.015%</td>
<td>0.004%</td>
</tr>
</tbody>
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How are LSPR sensors made for H$_2$ detection?

Evaporation of (0.2nm) Pd on Au

Atmospheric Pressure (1 atm)

Room temperature (20°C)

More sensitive with Pd on Au

1 nm Pd on Au

Better with more Pd

Error gas p(H$_2$) ≈ 10%
How are LSPR sensors made for H\textsubscript{2} detection?

Evaporation of (0.2nm) Pd on Au

Error gas p(H\textsubscript{2}) \approx 10%

0.004%

0.015%

0.06%

0.25%

More sensitive with Pd on Au

0.001%

0.0002%

1 nm Pd on Au

Better with more Pd

With our sensitivity is Au indispensable?
Anisotropic Pd samples: OAD

Anisotropy in the TAS spectrum

Dichroism

Model the anisotropy of Pd

- Calculated with effective medium theory

\[
\varepsilon_x(\omega) = f\varepsilon(\omega) + (1-f)\varepsilon_m
\]

\[
\varepsilon_y(\omega)^{-1} = f\varepsilon(\omega)^{-1} + (1-f)\varepsilon_m^{-1}
\]


Reproduces the **position** but **not** the **width**
Model the anisotropy of Pd

- Calculated with effective medium theory


Enables calculation of the hydrogenation
Effect of hydrogenation on Pd

Exposure to H₂ : spectrum

Calculation of the hydrogenation

\[ \frac{x}{2} \left( H_2 (g) + xPd \rightarrow PdH_x \right) \]

\[ x = \frac{H}{Pd} : \text{Degree of hydrogenation} \]


**Strong damping of the anisotropy due to hydrogenation of Pd**
H₂ & Ar cycles with Pd sensor

**H₂ & Ar cycles with Pd sensor**

- $p(H₂) ≫ 1% ⇒ β$
- $p(H₂) ≈ 1% ⇒ α + β$
- $p(H₂) ≪ 1% ⇒ α$

Strong $ΔS$ change

- $p(H₂) ≫ 1%$

$β$ phase – dense

**H₂ & Ar cycles with Pd sensor**

Strong $\Delta S$ change

- $p(H₂) \gg 1\% \Rightarrow \beta$
- $p(H₂) \approx 1\% \Rightarrow \alpha + \beta$
- $p(H₂) \ll 1\% \Rightarrow \alpha$

$\beta$ phase – dense

Weak $\Delta S$ change

- $p(H₂) \ll 1\%$

$\alpha$ phase – dilute

H₂ & Ar cycles with Pd sensor

- Strong ΔS change: \( p(H_2) \gg 1\% \Rightarrow \beta \)
  - \( \beta \) phase – dense
- Slow ΔS change: \( p(H_2) \approx 1\% \)
  - \( \alpha + \beta \) phase
- Weak ΔS change: \( p(H_2) \ll 1\% \)
  - \( \alpha \) phase – dilute

Thermodynamic: phase diagram (isotherm)

Origin of the drop in $\Delta S$

- $\Delta S$

Can we get a quantitative measurement?

- Quantitative measurement!

### Thermodynamic: Comparison to Lit.

**Quantitative measurement!**

```
\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Ref. & Detection limit & Carrier gas & Response time [s] \\
\hline
\hline
 & 4\% & *Ar* & 50 \\
\hline
\hline
\hline
\hline
\end{tabular}
\caption{Values from the literature: LSPR with Au & Pd}
\end{table}
```

**Most sensitive** LSPR measurements of H₂

Values from the literature: LSPR with Au & Pd

<table>
<thead>
<tr>
<th>Ref.</th>
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<th>Carrier gas</th>
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<tbody>
<tr>
<td>&quot;</td>
<td>4%</td>
<td>Ar</td>
<td>50</td>
</tr>
<tr>
<td>A. Yang, et al, (2013), ACS Nano, 8, 8, 7639–7647</td>
<td>2%</td>
<td>N₂</td>
<td>180</td>
</tr>
</tbody>
</table>

Kinetic: 2 time responses

$t_{90}$
Reach 90% of signal

$t_{\text{detect}}$
Reach readable of signal

Kinetic: In the $\beta$-phase

$t_{90}$
Reach 90% of signal

<table>
<thead>
<tr>
<th>$p(\text{H}_2)$</th>
<th>$t_{90}$</th>
<th>$t_{\text{detect}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4% $\beta$-phase</td>
<td>32 s</td>
<td>$\leq 0.6$ s</td>
</tr>
<tr>
<td>0.25% $\alpha$-phase</td>
<td></td>
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$t_{\text{detect}}$
Reach readable of signal

Kinetic: In the \( \alpha \)-phase

\[
\text{\( t_{90} \)}
\]
Reach 90% of signal

<table>
<thead>
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<th>( t_{\text{detect}} )</th>
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<td>4% ( \beta )-phase</td>
<td>32 s</td>
<td>( \leq 0.6 ) s</td>
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<tr>
<td>0.25% ( \alpha )-phase</td>
<td>40 s</td>
<td>( \leq 1 ) s</td>
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Kinetic: In the $\alpha$-phase

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The faster the better!

Could we make it faster?

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<td>50</td>
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</table>
### Kinetic study : Setup

#### Absorption

<table>
<thead>
<tr>
<th>H/Pd (x 10^-2)</th>
<th>Time [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25%</td>
<td></td>
</tr>
<tr>
<td>0.06%</td>
<td></td>
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<tr>
<td>0.015%</td>
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</tbody>
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Absorption kinetic **dependent** of initial \( p(H_2) \)

#### Desorption

<table>
<thead>
<tr>
<th>( \Delta S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Only consider 0.25%</td>
</tr>
</tbody>
</table>

Desorption kinetic **independent** of initial \( p(H_2) \)
Kinetics: How does it behave?

**Absorption**
- $H/Pd = 3.5$ at $0.25\%$
- $H/Pd = 3.0$ at $0.06\%$
- $H/Pd = 2.5$ at $0.015\%$
- $H/Pd = 2.0$ at $0.004\%$
- $H/Pd = 1.5$ at $0.001\%$

**Desorption**
- $H/Pd = 3.5$ at $0.25\%$

Kinetic *expressed* in terms of $H/Pd$
Reaction mechanism

\[ \begin{align*}
H_2(g) + 2S & \xrightleftharpoons[\kappa_{des}]{\kappa_{ads}} 2H - S \\
H - S + V & \xrightleftharpoons[\kappa_{emp}]{\kappa_{abs}} H - V + S
\end{align*} \]

- **θ** : surface coverage
- **α** : volume H/Pd

- **Adsorption** on the surface \( r_{ads} = k_{ads} p (1 - \theta)^2 \)
- **Desorption** from the surface \( r_{des} = k_{des} \theta^2 \)
- **Absorption** in volume \( r_{abs} = k_{abs} \theta (1 - \alpha) \)
- **Emptying** from the volume \( r_{emp} = k_{abs} (1 - \theta) \alpha \)

Equations to solve to find \( \alpha(t) \)

\[ \frac{d\theta}{dt} = r_{ads} - r_{des} - r_{abs} + r_{emp} \]

\[ \frac{d\alpha}{dt} = r_{abs} - r_{emp} \]
Kinetics: fitting the data

\[ \theta : \text{surface coverage} \quad \alpha : \text{volume H/Pd} \]

Model fits all kinetics simultaneously

Fitted values:
- \( k_{ads} = 1.11 \cdot 10^{-2} \text{ mbar}^{-1} \)
- \( k_{des} = 0.235 \text{ s}^{-1} \)
- \( k_{abs} = 0.214 \text{ s}^{-1} \)
- \( k_{emp} = 0.111 \text{ s}^{-1} \)

Equation set:
\[
\begin{align*}
\text{H}_2(g) + 2S & \xrightarrow{k_{ads}} 2H - S \\
H - S + V & \xrightarrow{k_{des}} H - V + S \\
\end{align*}
\]

- \( r_{ads} = k_{ads} \theta (1 - \theta)^2 \)
- \( r_{des} = k_{des} \theta^2 \)
- \( r_{abs} = k_{abs} \theta (1 - \alpha) \)
- \( r_{emp} = k_{abs} (1 - \theta) \alpha \)

\[
\begin{align*}
\frac{d\theta}{dt} &= r_{ads} - r_{des} - r_{abs} + r_{emp} \\
\frac{d\alpha}{dt} &= r_{abs} - r_{emp}
\end{align*}
\]
**Kinetics: fitting the data**

\[ \frac{1}{H/Pd}(t) \]

- **\( \theta \): surface coverage**
- **\( \alpha \): volume H/Pd**

**H/Pd**

**Equation set**

\[ H_2(g) + 2S \underset{k_{des}}{\xrightarrow{k_{ads}}} 2H - S \]
\[ H - S + V \underset{k_{emp}}{\xrightarrow{k_{abs}}} H - V + S \]

- \( r_{ads} = k_{ads} \theta (1 - \theta)^2 \)
- \( r_{des} = k_{des} \theta^2 \)
- \( r_{abs} = k_{abs} \theta (1 - \alpha) \)
- \( r_{emp} = k_{abs} (1 - \theta) \alpha \)

**Desorption limited by surface**
**Kinetics: fitting the data**

θ: surface coverage  α: volume H/Pd

**Equation set**

\[
\begin{align*}
\text{H}_2(\text{g}) + 2S & \xrightarrow{k_{\text{ads}}} 2\text{H} - S \\
\text{H} - S + V & \xrightarrow{k_{\text{abs}}} \text{H} - V + S \\
\end{align*}
\]

- \( r_{\text{ads}} = k_{\text{ads}} \theta^2 (1 - \theta) \)
- \( r_{\text{des}} = k_{\text{des}} \theta^2 \)
- \( r_{\text{abs}} = k_{\text{abs}} \theta (1 - \alpha) \)
- \( r_{\text{emp}} = k_{\text{abs}} (1 - \theta) \alpha \)

**Absorption limited by volume**

**Desorption limited by surface**
**Kinetics: What do we learn?**

- Desorption limited by **surface**
  - ✔️ Self regenerates

- Absorption limited by **volume**
  - ✗ Improvement $t_{90}$ difficult
    - Limited by chemistry of Pd
Use in real world conditions

Effect of O₂ on Pd

Strong effect of O₂ on dielectric function of Pd

Effect of air & H₂O (4% H₂ in air | 50% humidity)

Still reactive in dry & humid air (4%)

Unreactive when left in air
Conclusion

Q With our sensitivity is Au indispensable?

High sensitivity reached in the α phase even with only Pd

Q Could we make it faster?

Kinetics limited by Pd / H₂ chemistry

Practical achievements
- High sensitivity
- Auto regenerates
- Wide range of p(H₂)
- Rapid response time
- Works in air

Fundamental achievements
- Quantitative reading in the α phase
- Limited by the phase diagram of Pd
- Kinetics limited by the Pd chemistry

PERSPECTIVES
Use of Metal Organic Frameworks as filters

Nano porous protective layer

- **Choice**: ZIF-8
  - \[ \text{Zn(NO}_2\text{)}_2 + \text{imidazole} \]
  - Zinc nitrate + imidazole

- **Expectations**:
  - Permeable to \( H_2 \) and **not** \( O_2 \) nor \( H_2O \)

Use of Metal Organic Frameworks as filters

**MOF in air cycles**

Cycles in dry air

Cycles after multiple days

Different mechanism in air…

Does not prevent oxidation of sample, but still sensitive

…but still reactive
Application in liquid medium

Fabrication of liquid cell

Direct industrial application

May be used for other type of sensing ex: protein, heavy metals, etc…
CONCLUSION
Summary and conclusion

**Techniques**

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAS</td>
<td>Single wavelength monitoring</td>
</tr>
<tr>
<td>OAD</td>
<td>Simple &amp; effective anisotropic samples</td>
</tr>
</tbody>
</table>

**Capabilities**

**Fundamental**
- Enables **fundamental investigation** of surface reactivity ideal for **catalysis**

**Application**
- **Direct application**: H₂ sensing
- But also: **biochemistry**, **green chemistry**

**Patent**: FR1859255
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