FUNDAMENTAL UNDERSTANDING OF SELECTIVE HYDROGENATIONS

Núria López
Hydrogenations: at the basis of catalysis

<table>
<thead>
<tr>
<th>Compound</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkene, R₂C=CR'₂</td>
<td>alkane, R₂CHCHR'₂</td>
</tr>
<tr>
<td>alkyne, RCCR</td>
<td>alkene, cis-RHC=CHR'</td>
</tr>
<tr>
<td>aldehyde, RCHO</td>
<td>primary alcohol, RCH₂OH</td>
</tr>
<tr>
<td>ketone, R₂CO</td>
<td>secondary alcohol, R₂CHOH</td>
</tr>
<tr>
<td>ester, RCO₂R'</td>
<td>two alcohols, RCH₂OH, R'OH</td>
</tr>
<tr>
<td>imine, RR'CNR&quot;&quot;</td>
<td>amine, RR'CHNHR&quot;&quot;</td>
</tr>
<tr>
<td>amide, RC(O)NR'₂</td>
<td>amine, RCH₂NR'₂</td>
</tr>
<tr>
<td>nitrile, RCN</td>
<td>imine, RHCNH</td>
</tr>
<tr>
<td>nitro, RNO₂</td>
<td>amine, RNH₂</td>
</tr>
</tbody>
</table>

Activity is important but SELECTIVITY is mandatory
Tools

Multiscale modeling framework for catalytic processes that exhibit strong coupling between scales.
What can we do?

**ATOMISTIC**
- Predict structure solids

**THERMODYNAMICS**
- Thermodynamics of processes
- Most-likely configurations under rx

**KINETICS**
- Reaction paths
- Kinetics processes
- Most-likely configurations under rx

**ENGINEERING**
- Store and search for data
- Identify structure-activity correlations
- Assess stability
- In-silico Design systems with specific properties
Gold chemistry and hydrogenation

\[ \text{C}_3\text{H}_4: \text{H}_2: \text{He} = 5:15:80 \]

0.2 wt.% Pd/Al_2O_3

\[ \text{X} \]

\[ \text{S(C}_3\text{H}_6) \]

General descriptor thermodynamic selectivity

F. Studt, F. Abild-Pedersen, T. Bligaard, R. Z. Sørensen, C. H. Christensen, J. K. Nørskov
Science, 320 1320 (2008)
Industrial problem: Alkyne hydrogenation

Cracking reactions

Fuel gas
Hydrogen

Steam Cracking or other Olefin Sources

C₂
Selective Hydrogenation

Dimerization
1-Butene

Oligomerization
Alpha-olefins

Metathesis
Ethene

C₃
Selective Hydrogenation

2-Butenes

Propene

Pd (~0.04%)/ δ-Al₂O₃
CO feeding (50-500 ppm)
T ~ 350 K
p ~ 20 bar

S alkenes
over-hydrogenation oligomomerisation
Hydrogenations: the problem
Hydrogenation: Reaction mechanism

C\textsubscript{2}H\textsubscript{2}(g) \rightleftharpoons HC\equiv CH \xrightarrow{H} HC\equiv CH_{2} \xrightarrow{H} \underline{\text{formation}}

\text{CH}_{3}

C

\underline{\text{formation}}

\underline{\text{formation}}

\underline{\text{formation}}

H\equiv CH_{2}

\text{H}_{2}C\equiv CH_{2}

\text{C}_{2}H_{4}(g)

\text{C}_{2}H_{6}(g)

Alkyne hydrogenation: Pd catalyst

Pd (~0.04%)/ Al₂O₃

Experimental evidence

Pretreatment → State of Pd → Sₘₐ𝑙ₗₜₜₜ

Self-consistently analyze composition activity

\[ \rho_{H_2}, \rho_{C_2H_2}, \rho_{CO}, X, S_{alkenes} \]
Hydride formation

**β-Hydride phase formation: BET equivalence**

- The adsorption takes place on a lattice
- First adsorbate layer is adsorbed on the solid surface
- Second adsorbate layer is adsorbed on the first
- Adsorption enthalpy first layer and then for other layers

\[
\frac{V_T(H)}{V_{1ML}(H)}
\]
Hydride formation

Pretreatment and State of Pd

$E_{ads} \sim -0.5 \text{ eV/atom}$

$E_{ads} \sim -0.1 \text{ eV/atom}$
Carbide formation

Pretreatment State of Pd

Carbide formation

Pretreatment and State of Pd

Dehydrogenations are lower in energy
C-C splitting lower at steps

Carbide formation

Pretreatment and State of Pd

- Lateral repulsion between C atoms is very large no dense phases PdC$_{0.13}$
- Preferential decoration of corners and steps, due to high formation energies at surfaces
- Near surface carbides, mostly
- Ability to be formed depends on the alkyne-alkene pair

Hydride formation in the presence of carbide

Pretreatment and State of Pd

\[
\frac{V_T(H)}{V_{1\text{ML}}(H)} > 1
\]

1 ML

Carbide prevents hydride formation

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>H/Pd ratio (± absolute uncertainty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In H₂*</td>
<td>0.75 (0.08)</td>
</tr>
<tr>
<td>In H₂ after hydrogenation events</td>
<td>0.87 (0.09)</td>
</tr>
<tr>
<td>Unselective hydrogenation†</td>
<td>0.92 (0.10)</td>
</tr>
<tr>
<td>Selective hydrogenation 1‡</td>
<td>0.18 (0.06)</td>
</tr>
<tr>
<td>Selective hydrogenation 2§</td>
<td>0.72 (0.10)</td>
</tr>
</tbody>
</table>
Alkyne hydrogenation: Pd catalyst

- **Industrial conditions**
  - Pd (~0.04%)/ δ-Al₂O₃
  - continuous CO feeding (50 < CO < 500 ppm)
  - T ~ 350 K
  - p ~ 20 bar
Role of CO: hydride formation

Pretreatment and State of Pd

- Very dense layers
- \( E_{\text{ads}} \approx -1.43 \text{ eV/atom} \)
  
  (\( p(2x2)\)-3CO)

CO prevents hydride formation
Reaction paths and kinetic contributions

Horiuti, J. and Polanyi, M.,
Kinetics pure Pd(111)

Pd clean surface

\[ E_a (eV) \]

- Ethyne: \[ E_{ads} = -2.02 \text{ eV} \]
- Ethene: \[ E_{des} = 0.82 \text{ eV} \]
- Ethyl: \[ 0.74 \]
- Ethylidene: \[ 0.79 \]
- Ethane: \[ 0.45 \]

Vinyl

- 0.81
- 0.79

50% vinyl

50% vinyl
Kinetics $\beta$-PdH

Experimental evidence

- $p_{H_2}$ pretreatment
- $T = 348K$
- $p = 1$ bar

Pd $/\gamma$-Al$_2$O$_3$

$E_a (eV)$

- $E_{ads} = -0.94$ eV
- $E_{des} = 0.15$ eV

Chemical reactions:

- Ethyne $\rightarrow$ Vinyl
- Ethene $\rightarrow$ Ethylidene
- Ethane $\rightarrow$ Ethane

Graph showing the distribution of ethanes, soligomers, and sethanes.
Kinetics b-PdH

Pd hydride

E_{ads} -0.94 eV

E_a(eV)

E_{des} 0.15 eV

ethyne

0.58

vinyl

0.36

ethene

0.75

ethylidene

0.06

HC-CH_{3}

PdH induces

S_{ethanes}

Experimental evidence

\bullet p_{H_2} pretreatment

\chi

X, S, \%

S_{oligomers}

S_{ethanes}
Kinetics Carbide phase

Carbide induce

$E_a (eV)$

$E_{\text{ads}}$ -1.49 eV

0.70

vinyl

0.57

0.69

Carbide induces $S_{\text{ethenes}}$

Experimental evidence

Carbide induces

$E_{\text{des}}$

0.67 eV

pH$_2$, pC$_2$H$_2$

pretreatment

$p_{H_2}$, $p_{C_2H_2}$

pretreatment

0.89

0.57

0.57

0.69

Sethenes

Soligomers

Sethanes

ethene

HC=CH$_2$

HC-CH$_3$

HC-CH$_3$

H$_2$C-CH$_3$

H$_3$C-CH$_3$

ethyl

ethane

Edes

0.67 eV

Eads

-1.49 eV

Carbide

Ethyne

Ethene

Ethylidene

Ethane

Edes

0.67 eV

0.70

0.57

0.69

0.89

0.57
Kinetics CO phase

- Ethyne (Eads = -1.24 eV)
- Ethene
- Vinyl
- Ethylidene
- Ethyl
- Ethane

$E_a (eV)$
$E_{des} = 0.00 eV$

$0.45, 0.14, 0.23, 0.44, 0.57, 0.20$
Kinetics CO phase

CO

\[ \text{Ethyne} \]

\[ \text{Vinyl} \]

\[ \text{Ethyl} \]

\[ \text{Ethylidene} \]

\[ \text{Ethane} \]

E_{\text{ads}} \quad -1.24 \text{ eV}

E_{\text{des}} \quad 0.00 \text{ eV}

E_{\text{ads}} \quad 0.45

E_{\text{des}} \quad 0.14

E_{\text{ads}} \quad 0.23

E_{\text{des}} \quad 0.44

E_{\text{des}} \quad 0.57

E_{\text{des}} \quad 0.20

CO induces \( S_{\text{ethenes}} \)

Experimental evidence

- Pretreatment

\[ \text{CO} \] induces \( E_{\text{ads}} \) -1.24 eV

\[ \text{CO} \] covered

\[ \text{H}_2\text{C-CH}_3 \]

\[ \text{H}_3\text{C-CH}_3 \]

\[ \text{H}_2\text{C-CH}_3 \]

\[ \text{HC-CH}_3 \]

\[ \text{HC=CH}_2 \]

Experimental data

\[ p_{\text{H}_2} \quad p \]

\[ p_{\text{C}_2\text{H}_2} \quad p \]
Oligomerization

\[ E_a = 1.38 \text{ eV} \]
\[ E_a(\text{+CO}) = 1.40 \text{ eV} \]

Reduction of ensembles
Oligomerization

$E_a = 1.38 \text{ eV}$

$E_a(+CO) = 1.40 \text{ eV}$

Reduction of ensembles
Requirements for a good hydrogenation catalyst

1. Thermodynamic selectivity
   Blocks subsequent reactions

2. No active subsurface species
   Blocks overhydrogenation
   Reduces oligomerization

3. Small ensembles

Carbide:
- Fulfills (1-3)
- Labile
- Difficult homogeneously

Hydride:
- Fulfills (1) and (3)

CO phase:
- Fulfills (1-3)
- Robust
- Easily homogeneous
- Overwrites the state of the catalyst

Hydrogenations: Technical solution

- Active metal
- Secondary metal
- Molecular Modifier
Role of co-catalyst

Complex substrates on Pd

1. Thermodynamic selectivity
2. Inability to form active subsurface species
3. Definition of small ensembles
Organic synthesis: Pd Lindlar Catalyst (1952)

Selective for Multifunctionalized Acetylenic molecules (Solvent)

\[
\text{BaSO}_4 + \text{Pd} \rightarrow \text{Pd/BaSO}_4 + \text{Pb(ACO)}_2
\]

95°C

Pb-Pd/BaSO₄ +

Vitamin A (Retinol)

Lindlar Catalyst
## Comparison between Pd catalysts

<table>
<thead>
<tr>
<th></th>
<th>Hydrorefining Catalyst</th>
<th>Lindlar Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Substrate</strong></td>
<td>Ethyne, propyne</td>
<td>Long chain alkynes</td>
</tr>
<tr>
<td><strong>Medium</strong></td>
<td>Gas phase or liquid phase</td>
<td>Liquid phase</td>
</tr>
<tr>
<td><strong>Pd content</strong></td>
<td>0.01 – 0.05 %</td>
<td>1 – 5 %</td>
</tr>
<tr>
<td><strong>Second metal</strong></td>
<td>Ag, Au, etc.</td>
<td>Pb, Bi, Cu</td>
</tr>
<tr>
<td><strong>Selectivity modifier</strong></td>
<td>CO</td>
<td>Quinoline</td>
</tr>
<tr>
<td><strong>Support</strong></td>
<td>Al₂O₃</td>
<td>CaCO₃, BaSO₄</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>RT – 350 K</td>
<td>RT</td>
</tr>
<tr>
<td><strong>Solvent</strong></td>
<td>None</td>
<td>Benzene, Toluene, Methanol</td>
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<tr>
<td><strong>Regioselectivity</strong></td>
<td>---</td>
<td>Cis</td>
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<tr>
<td><strong>P_H₂</strong></td>
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<td><strong>Operation</strong></td>
<td>Continuous</td>
<td>Batch</td>
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Lindlar preparation: I
Lindlar preparation: II

$\text{Pb(AcO)}_2$ at 95ºC

Formation of Pb islands

$E_{isl}$

Unfavourable
Lindlar preparation: III

Lindlar Tiling

Jujol, Gaudi 1906
Lindlar Tiling

Thermodynamic selectivity

Blocks subsequent reactions
Lindlar Tiling

Inability to form hydride

Achieved by tiles (solvent)
Lindlar Tiling

**Definition of small ensembles**

Reduces oligomerization

Garcia-Mota et al. TCA 128, 663 (2011)
New generation catalyst: supported colloids

BASF NanoSelect™ technology

metal salt + HHDMA → metal colloid

- Reducing and stabilizing function combined in one reagent
- Hexadecyl(2-hydroxyethyl)-dimethylammonium dihydrogenphosphate

- Water-soluble, air-stable, BASF compound
EP08150726.1-2104
Preparation of ligand-modified catalysts

- NanoSelect™ technology
  - Easy to scale up
  - No centrifugation required
  - Versatile

- Conventional technique
  - Difficult to scale up
  - Low-boiling point compounds
  - Centrifugation required

Witte, Patent NL50039, 2009 • Witte et al., ChemCatChem 5, 582 (2013)
The structure: TEM
## Comparison between Pd catalysts

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<th>Lindlar Catalyst</th>
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<td>TiS</td>
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<td>Continuous</td>
<td>Continuous</td>
<td>Batch</td>
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</table>
State-of-the-art alkyne hydrogenation catalyst BASF

Lindlar Drawbacks:

- Poor metal utilization
- Lead as a modifier

Structure of the ligand-modified catalyst

Cryo-TEM

TGA

ToF-SIMS

$^{31}$P MAS NMR
The interface structure
Textural and compositional characterization

### Palladium

- **0.5 wt.% Pd or Pt HHDMA/C**
- Image with text: 
  - 231 m² g⁻¹
  - $D = 17\%$

- **5 wt.% Pd or Pt**
- Image with text: 
  - 10 m² g⁻¹
  - $D = 6\%$

### Platinum

- **1-4 wt.% Pb/CaCO₃**
- Image with text: 
  - 234 m² g⁻¹
  - $D = 49\%$

- **10 nm**
- Image with text: 
  - 4 m² g⁻¹
  - $D = 8\%$

Pd-HHDMA in alkyne hydrogenation

1-hexyne hydrogenation

$W_{\text{cat}} = 0.1 \, \text{g}$, $T = 30^\circ \text{C}$, $P = 1 \, \text{bar}$

$F(H_2) = 18-36 \, \text{cm}^3 \, \text{min}^{-1}$

$F(C_6H_{10} + \text{solv.}) = 0.3-3 \, \text{cm}^3 \, \text{min}^{-1}$

Facile -NO₂ adsorption and H₂ activation enhance the activity of Pt-HHDMA

ACS Catal. 2015, 5, 3767
All strategies are based on

Large amount of Pd

Poisoned in some way

Is it possible to use the minimum ensemble without poisoning
mpg-C$_3$N$_4$ support


*Angew. Chem., Int. Ed.* 2015, doi: 10.1002/anie.201505073R1
Single site hydrogenation catalyst

Active 1-hexyne
Selective
Stable

Angew. Chem., Int. Ed. 2015, doi: 10.1002/anie.201505073R1
Single site hydrogenation catalyst

Active 1-hexyne
- mechanism as homogeneous Pd
- thermodynamic selectivity
- Stable
- low Pd concentration in pores

*Angew. Chem., Int. Ed.* 2015, doi: 10.1002/anie.201505073R1
Conclusions

• Integration of DFT and experiments is crucial to understand the chemistry

• The strategies in Pd chemistry for hydrogenation are the same independently application

• Reduction of the catalyst to smallest ensemble is possible
Acknowledgements

M. Garcia-Mota
G. Novell-Leruth
C. Vargas-Fuentes
L. Bellarosa
N. Almora-Barrios

Experimental Collaborations

Prof. J. Pérez-Ramírez (ETH)
G. Vilé
CeO$_2$: Oxygen Vacancy formation

CeO$_2$ is able to reversible adsorb O$_2$ in volume

Bulk vacancies more stable than surface ones


Fig. 2. Calculated relationship between ln(y) and ln(PO$_2$) in the CeO$_2$–CeO$_{1.5}$ system at different temperatures, together with the experimental data of [19].
CeO$_2$: STM images localization and islanding

Annealing 900$^\circ$C 5 min

<table>
<thead>
<tr>
<th></th>
<th>RuO$_2$</th>
<th>CeO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl Coverage</td>
<td>↑↑↑↑↑</td>
<td>↑↑</td>
</tr>
<tr>
<td>Mechanism</td>
<td>2D</td>
<td>2D-3D</td>
</tr>
<tr>
<td>Largest $E_a$</td>
<td>Cl$^<em>$+Cl$^</em>$→Cl$_2$+2*</td>
<td>Cl# +Cl$^<em>$→Cl$_2$+#+</em></td>
</tr>
<tr>
<td>Key step</td>
<td>O$_2$ adsorption</td>
<td>O$_2$ adsorption</td>
</tr>
</tbody>
</table>
$\beta$-Hydride phase formation: BET equivalence

\[ H_2^{gas} + 2^* \leftrightarrow 2H^*(1) \]

\[ k_{1,H_2} p_{H_2} \Theta_0^2 = k_{-1,H_2} \Theta_1^2 \]

\[ H_2^{gas} + 2(1) \leftrightarrow 2H^*(2) \]

\[ k_{i,H} p_{H_2} \Theta_i^2 = k_{-i,H} \Theta_i^2 \]

\[ H_2^{gas} + 2(i-1) \leftrightarrow 2H^*(i) \]

\[ V = V_0 \sum_{i=0}^{\infty} i \Theta_i \]

\[ A = A_0 \sum_{i=0}^{\infty} \Theta_i \]

\[ \frac{V_T(H)}{V_{1ML}(H)} \]
\[ \frac{V_T(H)}{V_{1ML}(H)} = \frac{cX}{(1 - X)(1 - X + cX)} \]

\[ c = \frac{Y}{X} = \left( \frac{K_1}{K_2} \right)^{\frac{1}{2}} \]

\[ Y = \left( \frac{K_{1,H_2}}{p_{H_2}} \right)^{\frac{1}{2}} \quad K_1(T) = \exp\left( \frac{-\Delta G_1^0}{k_BT} \right) \]

\[ X = \left( \frac{K_{2,H_2}}{p_{H_2}} \right)^{\frac{1}{2}} \quad K_2(T) = \exp\left( \frac{-\Delta G_2^0}{k_BT} \right) \]

\[ \frac{V_T(H)}{V_{1ML}(H)} > 1 \quad \rightarrow \quad \text{Hydride Pd} \]
Role of the molecular modifier

Continuous CO feeding (50 < CO < 500 ppm)

Reaction paths: Thermodynamic factor

Activation and reaction energies are linked by a BEP-like relationship.

**BEP-relationships**

![Graph showing activation energies vs. reaction energies for different compounds](image)
Activity of Colloidal Pd, Pt nanoparticles
Cu can be attractive under some conditions but … requires higher T and generates more oligomers

Carbide exclusion area

Pretreatment and State of Pd

• Large exclusion areas around C species