Hydrogenation:
Basics and Examples

Detre Teschner
What is hydrogenation?

\[
\text{CH}_3\text{CH}_3 + \text{H}_2 \rightarrow 2\text{CH}_4
\]

\[
\boxed{\text{CH}_2\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_3}
\]

\[
\text{c-C}_5\text{H}_{10} + \text{H}_2 \rightarrow \text{C}_5\text{H}_{12}
\]

\[
\text{CD}_2\text{CD}_2 + \text{H}_2 \rightarrow \text{CD}_2\text{CDH} + \text{HD}
\]
Possible ways of hydrogenation?

- Heterogeneous catalytic: over metals
- Heterogeneous catalytic: over non-metals
- Homogeneous catalytic: metal complexes
- Chemical reduction: with diimide, LiAlH₄
- “Ionic hydrogenation”: with protic acid and hydride ion donor
Application

- Petrochemical applications
- Food industry
- Pharmaceutical industry
- Chemical synthesis

<table>
<thead>
<tr>
<th>Industry</th>
<th>Molecular weight of product/g mol(^{-1})</th>
<th>Synthetic steps to product</th>
<th>Production/t a(^{-1})</th>
<th>kg by-product per kg product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base chemicals</td>
<td>&lt;50</td>
<td>1–2</td>
<td>(10^4–10^4)</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Bulk chemicals</td>
<td>50–100</td>
<td>1–5</td>
<td>(10^4–10^6)</td>
<td>&lt;1–5</td>
</tr>
<tr>
<td>Fine chemicals</td>
<td>100–300</td>
<td>5–10</td>
<td>(10^2–10^4)</td>
<td>5–&gt;50</td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>100–1000</td>
<td>&gt;10</td>
<td>(10^0–10^3)</td>
<td>25–&gt;100</td>
</tr>
</tbody>
</table>
A homogeneous mechanism

Wilkinson catalyst
A homogeneous mechanism

Wilkinson catalyst
Basics: L.-H.; H.-P.;


Berlin 29.01.10.
Basics: Syn stereochemistry

Both H adds from the same face of the functional group
Newns–Anderson model of interaction in an adsorption system with a semi-elliptic DOS band (gray) at the surface and a deltafunction DOS on the adsorbate before the interaction. The resulting adsorbate state projected DOS (blue) takes a number of forms depending on the parameters. (a) Increasing the bandwidth, (b) Increasing the interaction strength, (c) Increasing the energy splitting, |Ed-Ea|.
Basics: H-M

Additional complexity: particle size, low coordination sites, strain, etc.

Basics: H in Pd

Special character of surface/subsurface/bulk H:
- Adsorption energy
- Sticking probability
- Reactivity
### Basics: What metals for which reaction?

#### Chemoselectivity

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Catalyst</th>
<th>Reaction medium</th>
<th>p/bar</th>
<th>T/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_2C=CR_2 \rightarrow R_2CH=CHR_2$ ($R = H, alkyl, aryl$)</td>
<td>Pd, Pt, Ni</td>
<td>Slightly polar</td>
<td>3–100</td>
<td>5–100</td>
</tr>
<tr>
<td>$RC=CR \rightarrow RCH=CHR$ ($R = H, alkyl, aryl$)</td>
<td>Pd</td>
<td>Slightly polar</td>
<td>1–3</td>
<td>5–50</td>
</tr>
<tr>
<td>$R_2CO \rightarrow R_2CHOH$ ($R = alkyl$)</td>
<td>Pt, Ni, Ru</td>
<td>Polar</td>
<td>1–10</td>
<td>50–150</td>
</tr>
<tr>
<td>$RCHO \rightarrow RCH_2OH$ ($R = alkyl$)</td>
<td>Pt, Ni, Ru</td>
<td>Polar</td>
<td>1–10</td>
<td>20–100</td>
</tr>
<tr>
<td>$ArCOR \rightarrow ArCH(OH)R$ ($Ar = aryl, R = alkyl$)</td>
<td>Pd, Ni, Pt</td>
<td>Slightly polar</td>
<td>1–10</td>
<td>5–50</td>
</tr>
<tr>
<td>$RCN \rightarrow RCH_2NH_2$ ($R = alkyl, aryl$)</td>
<td>Ni</td>
<td>Ammonia</td>
<td>20–40</td>
<td>20–100</td>
</tr>
<tr>
<td>$RCH=NOH \rightarrow RCH_2NH_2$ ($R = alkyl, aryl$)</td>
<td>Pt, Pd</td>
<td>Polar + HCl</td>
<td>1–10</td>
<td>20–100</td>
</tr>
<tr>
<td>$R_2C=NR \rightarrow R_2CHNHR$ ($R = H, alkyl$)</td>
<td>Ni, Pt, Pd, Rh</td>
<td>Acidic</td>
<td>1–50</td>
<td>5–100</td>
</tr>
<tr>
<td>$RN_3 \rightarrow RNH_2$ ($R = alkyl, aryl$)</td>
<td>Pt, Ni</td>
<td>Polar</td>
<td>3–50</td>
<td>50–150</td>
</tr>
<tr>
<td>$RNO_2 \rightarrow RNH_2$ ($R = alkyl$)</td>
<td>Pd</td>
<td>Polar</td>
<td>1–10</td>
<td>20–50</td>
</tr>
<tr>
<td>$RX \rightarrow RH$ ($R = alkyl, X = Hal$)</td>
<td>Pd, Pt, Ni</td>
<td>Various</td>
<td>1–5</td>
<td>5–50</td>
</tr>
<tr>
<td>$RCH_2X \rightarrow RCH_3$ ($R = alkyl, X = Hal$)</td>
<td>Pd</td>
<td>Basic</td>
<td>1–10</td>
<td>50–100</td>
</tr>
<tr>
<td>$RCH=CHR$ ($R = alkyl, X = Hal$)</td>
<td>Pd</td>
<td>Basic</td>
<td>1–10</td>
<td>20–100</td>
</tr>
<tr>
<td>$RCOX \rightarrow RCHO$ ($R = alkyl, aryl, X = Hal$)</td>
<td>Pd</td>
<td>Acidic</td>
<td>1–10</td>
<td>20–100</td>
</tr>
<tr>
<td>$RCOOR \rightarrow RCH_2OH$ ($R = alkyl, aryl$)</td>
<td>Cu, Ru</td>
<td>Apolar</td>
<td>100–300</td>
<td>100–200</td>
</tr>
<tr>
<td>Ar $\rightarrow$ R ($R = saturated ring$)</td>
<td>Rh, Pt</td>
<td>Various</td>
<td>3–100</td>
<td>20–100</td>
</tr>
<tr>
<td>HeteroAr $\rightarrow$ R ($R = saturated heterocycle$)</td>
<td>Ru, Ni</td>
<td>Various</td>
<td>20–100</td>
<td>50–150</td>
</tr>
<tr>
<td></td>
<td>Pt, Pd</td>
<td>Acidic</td>
<td>20–50</td>
<td>50–150</td>
</tr>
<tr>
<td></td>
<td>Rh, Ru</td>
<td>Various</td>
<td>5–100</td>
<td>50–150</td>
</tr>
</tbody>
</table>

Handbook of Catalysis: p.3286.

Hydrogenation of functional groups

*Berlin 29.01.10.*
Basics: Sterical effects?

Hydrogenation rate:

- $\text{RCH} = \text{CH}_2 > \text{RCH} = \text{CHR}$
- Cis $>$ Trans
- Decreases with increasing substituents
### Basics: sterical effect, isomerization

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant, Products</th>
<th>% yield at reaction time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>Pd/SiO₂</td>
<td>1-Pentyne</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>1-Pentene</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>t-2-Pentene</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>c-2-Pentene</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Pentane</td>
<td>0</td>
</tr>
<tr>
<td>Pd/SiO₂</td>
<td>2-Pentyne</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>1-Pentene</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>t-2-Pentene</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>c-2-Pentene</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Pentane</td>
<td>0</td>
</tr>
</tbody>
</table>

Equilibrium: ~ 80% t-2-ene, 18% c-2-ene, 2%: 1-ene


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Question

Hydrogenation of tetra-substituted alkenes with relative ease?

Tetra substituted alkenes readily undergo saturation in ionic hydrogenation.

Why?
Basics: surface species

Proposed surface intermediates in hydrogenation of acetylene.

A. Borodzinski: hydrogenation between HC deposits
Example 1: subsurface H

Different response to $p(D_2)$

Example 1

Surface H for isomerization Subsurface H for hydrogenation


Example 1

Hydrogenation in the presence of subsurface H [Pd particles]

Pentenes to pentane

No hydrogenation without subsurface H [Pd(111)]

Example 2: structure sensitivity

1,3-butadiene hydrogenation

Example 3: ☀️ vs. 🌞 bond hydrogenation

Acetylene Hydrogenation to Ethylene over Pd(111)

Energy (kcal/mol)


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Example 3


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Example 3

For \( \text{C}_3\text{H}_4 \) the HOMO is situated \( \sim 0.4 \text{ eV} \) lower than the corresponding level of \( \text{C}_3\text{H}_6 \): larger coupling with the metal \( d \) states, and thus to larger binding energy to metallic particles.
Simulated surface coverages of the reaction intermediates for acetylene hydrogenation over Pd(111) at $\text{PC}_2\text{H}_2 = 100 \text{ Torr}$ and $\text{PH}_2 = 100 \text{ Torr}$

Example 3

\[
\begin{align*}
H_2(g) + 2* & \leftrightarrow H^* + H^* \\
C_2H_2(g) + * & \leftrightarrow C_2H_2^* \\
C_2H_2^* + H^* & \leftrightarrow CHCH_2^* + * \\
CHCH_2^* + H^* & \leftrightarrow C_2H_4^* + * \\
C_2H_4^* & \rightarrow C_2H_4(g) + * \\
C_2H_4^* + H^* & \leftrightarrow C_2H_5^* + * \\
C_2H_5^* + H^* & \rightarrow C_2H_6(g) + 2*
\end{align*}
\]

Example 3

1 ml 1-pentyne / 2 bar / 40°C

Concentration (M)

Time (mins)

1%Pd/Al$_2$O$_3$

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Example 3

1 ml cis pent-2-ene/2bar/40C with 1 ml 1-pentyne added after 1 hr

Concentration M

Time (mins)

1% Pd/Al₂O₃

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Example 3: effect of trans

1% Pd/Al₂O₃
Example 3

The heat of adsorption difference between alkyne and alkene can define selectivity.

Methyl heat of adsorption

Reaction coordinate

Example 3

Differential adsorption energy of a methyl group as a function of the carbon coverage as well as the Ag/Pd and H/Pd ratios. Red: palladium with subsurface carbon, blue: Pd-Ag alloys, green: palladium hydrides. Weakening of the adsorption energy of methyl groups should increase the selectivity towards ethylene.

Example 3

WRONG FOR H!!


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Intermezzo

Cis-2-pentenitrile

Trans-2-pentenitrile

Cis & trans-3-pentenitrile

Valeronitrile

Amylamine

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Intermezzo

Ni/Al2O3

fractional composition

Time on stream (mln)

C2PN  AA  VN  T2PN  T3PN

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Example 3: In-situ XPS: Pd 3d: sub-surface C

1-pentyne hydrogenation

unambiguous localisation of carbon-induced component in the surface-near region
BUT: not one layer

Hydride excluded
Example 3


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Example 3

alkynes: Pd-C
alkenes: no Pd-C


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Example 3

Graph showing the relationship between the logarithm of the pressure of $C_2H_2$ and the logarithm of the pressure of $C_2H_4$. The graph is divided into four regions (I, II, III, IV) based on the values of $\log p(C_2H_2)$ and $\log p(C_2H_4)$. The graph includes molecules $C_2H_4$ and $C_2H_2$.
Example 3
Example 3

![Graphs showing temperature and ln(P_{H2}/P) for PdH and Pd phases.](image)


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Example 3: H diffusion barriers

Example 3

Selective hydrogenation with Pd-C
Non-selective hydrogenation with Pd
Example 3

“Pd metal”  
(β-hydride)

“Pd-C”  
surface phase  
(h.p. XPS)

In situ PGAA

Hydrogenation

Quantitative determination of H uptake

Target

\( ^{A}_{Z}X \)

Neutron capture

Compound nucleus

\( ^{A+1}_{Z}X^* \)

Prompt-gamma radiation

\( ^{A+1}_{Z}X \)

Radioactive decay

\( ^{A+1}_{Z\pm 1}X^* \)

Decay gamma radiation

\( ^{A+1}_{Z\pm 1}X \)
Example 3: In situ PGAA

No correlation between activity and H/Pd in selective C$_5$H$_8$ hydrogenation, despite the first order p(H$_2$) rate dependence. Bulk is decoupled.

Exp. 1-4: identical conditions

Exp. 5-6: identical conditions
Example 3

Selective

Non-s.

Propyne hydrogenation: first order for $p(H_2)$
Example 3

![Graph showing H/Pd ratios for different hydrogen flow rates.]

Hₚ₃, 0 cm³ min⁻¹ H₂, 20 cm³ min⁻¹ H₂, 32 cm³ min⁻¹ H₂

Experiments

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Example 3

Kinetic discontinuity; oscillations

Adiabatic reactor

Control of selectivity: issue!

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Example: PdGa

$h\nu = 200$ eV

PdGa

BE / eV

Intensity / a.u.

Pd

DOS (states/eV/cell)

PdGa

DOS (states/eV/cell)

Pd

Energy (eV)
Question

DOS, VB of PdGa looks like…?

From slide 9…
Example: PdGa

- Isolated Pd site
- Covalent bonding
- Modified electronic structure

No H dissolution (PGAA)

Excellent selectivity in acetylene semi-hydrogenation
Example: PdGa


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Example: competitive reaction

over Pd/C

<table>
<thead>
<tr>
<th>Second component</th>
<th>Initial rates(^a) of hydrogenation(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phenyl acetylene</td>
</tr>
<tr>
<td>Phenyl acetylene</td>
<td>84.2</td>
</tr>
<tr>
<td>1-Phenyl-1-propyne</td>
<td>-</td>
</tr>
<tr>
<td>1-Pentyne</td>
<td>5.4</td>
</tr>
<tr>
<td>2-Pentyne</td>
<td>15.2</td>
</tr>
</tbody>
</table>

\(^a\) Rates in mmol g\(^{-1}\) min\(^{-1}\).

\(^b\) The table is symmetric about the diagonal axis for competitive reactions. The results on the axis are those for the compound in the absence of a second component. All other rates should be read “down”. For example the rate of 1-pentyne hydrogenation in the presence of 1-phenyl-1-propyne is 12.8, while the rate of 1-phenyl-1-propyne hydrogenation in the presence of 1-pentyne is 0.5.


Competitive reactions are sometimes difficult to predict!

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Example 4: Edible Oils

Edible oils (sunflower, soybean) consist of long chain fatty acids - C16 to C18.

Mixtures of saturated (SFA), mono (MFA) - and polyunsaturated (PFA) fatty acids.

MFA and PFA can exist in *cis* or *trans* configuration.

Research shows *trans* fatty acids (TFA) lead to high LDL cholesterol: BAD!
Example 4

- Palmitic Acid (C16)
- Stearic Acid (C18)
- Oleic Acid (C18:1)
- Linoleic Acid (C18:2)
- Linolenic Acid (C18:3)
Example 4

Hydrogenation of edible oils necessary to produce solid foods such as margarine, PFA, MFA

Isomerization of cis fatty acids to trans fatty acids can occur during hydrogenation

Development of hydrogenation catalysts which offer higher selectivity to products with cis configuration and lower selectivity towards SFA formation is of great commercial interest

**Nickel Systems**

- High TFA content 15-30%
- H₂ surface concn – Low = TFA
- High = SFA
- Low Temperature – Low TFA

**Platinum Systems**

- More active
- Lower TFA content (8%)
Example 5: Regioselectivity

Effect of “R”: steric hindrance
Example 5

![Graph showing selectivity vs. pressure for Ag/SiO$_2$.](image)
Selectivity control

Size of Ag terrace, Roughness of Ag, Pressure of acrolein
Example 6: $C_6H_6$ hydrogenation

Increasing $H_2$ partial pressure increases the selectivity of the partial hydrogenation product (cyclohexene)!

complex interplay of mass transfer limitations?

Figure 5: Influence of the hydrogen pressure on the course of the partial benzene hydrogenation. For clarity the profiles of cyclohexane are left out. Experimental conditions: 0.5 g Ru-B, 200 ml benzene, 150 ml water, 2.4 g iron sulfate, temperature 443 K, reactor I.

Soede: PhD thesis
Core-shell structure to avoid secondary reaction
Lindlar catalyst: Pd on CaCO$_3$ (non-porous!) deactivated with Pb and quinoline

Vitamin A synthesis

Gas-hold up is considerably higher for up-pumping than down-pumping PBT.

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1. Stirred vessel
2. Strobe lamp
3. Strobe flash
4. Stereo microscope
5. Video camera
6. Video recorder
7. TV monitor
8. Computer
9. Impeller

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The University of Birmingham
Engineering: bubble size

100% Water

100% IPA

65% IPA

1% IPA

5% IPA

30% IPA

The University of Birmingham

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Conclusion