Towards realistic systems

Karoliina Honkala
Department of Chemistry
Nanoscience Center
University of Jyväskylä
Finland

Content:
- d-band model
- BEP line
- Sabatier's principle
- Volcano curve
- Temperature and pressure gaps
- Compensation effect
- Lateral interactions
- etc
Complexity of models

Sabatier's principle:
The best catalysts have intermediate adsorbate-surface bond strengths.

Dissociate $N_2$ but $N$ binds too strongly.

Ozaki and Aika, *Catalysis* 1 (Anderson and Boudart, Ed.)
Brønstead-Evans-Polanyi (BEP) relationship

BEP relation states that the activation energy and reaction energy are linearly related for an elementary reaction.

Calculated activation energies on a number of different metals as a function of the calculated dissociative chemisorption potential energy for the dissociation products.

BEP relations for $\text{C}_2\text{H}_4$ dehydrogenation and hydrogenation on flat and stepped Pd

\[ \text{H}_2\text{CCH}_2 \ast \ast \leftrightarrow \text{HCCCH}_2 \ast \ast \text{H} \ast \]  
\[ \text{H}_2\text{CCH}_3 \ast \ast \leftrightarrow \text{H}_2\text{CCH}_2 \ast \ast \text{H} \ast \]  
\[ \text{H}_2\text{CCH}_3 \ast \ast \leftrightarrow \text{HCCCH}_3 \ast \ast \text{H} \ast \]  
\[ \text{HCCCH}_3 \ast \ast \leftrightarrow \text{HCCCH}_2 \ast \ast \text{H} \ast \]  
\[ \text{HCCCH}_3 \ast \ast \leftrightarrow \text{CCH}_3 \ast \ast \text{H} \ast \]  

J. Andersson et al. submitted
The d-band model

there are also many other good references.

The d-band model
★ combines the tight-binding approximation and the Newns-Anderson model.
★ is used to explain the variations in adsorption and activation energies from one transition metal to another by variations in the coupling between the levels of adsorbate and the d-band of transition metal.

Calculated C-H bond activation barriers for ethylene ($C_2H_4$) and ethyl ($C_2H_5$) on various surfaces.

V. Pallassana et al. J. Cat. 191,301,(2000)
\[ E_{\text{ads}} = E_{\text{sp}} + E_{\text{d-hyb}} \]

\( E_{\text{sp}} \) is the interaction of the adsorbate with the sp-band of the metal. \( E_{\text{d-hyb}} \) is the contribution due to the interaction of the adsorbate with the valence d-band. In the case the coupling is weak relative to the energy difference between the two states, \( E_{\text{d-hyb}} \) is

\[ E_{d-\text{hyd}} = -2(1-f) \frac{V^2}{|\epsilon_d - \epsilon_a|} + 2(1+f) \alpha V^2 \]

The 1'st term attractive if the d-band is not completely full. The 2'nd term is the Pauli repulsion.

\( \delta E_{\text{ads}} = E_{\text{sp}} + \delta E_{\text{d-hyb}} \) describes how the adsorption energy of an adsorbate \( A \) varies from one transition metal to the other. It is possible to show that

\[ \delta E_{d-\text{hyd}} \propto \delta \epsilon_d \]
Comparison of oxygen adsorption energies


C$_2$H$_4$ adsorption energies

The width can be decreased by straining the surface or creating a step or a kink.


<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
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<tbody>
<tr>
<td></td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
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<tr>
<td></td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
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</tbody>
</table>

The general rule: higher the d-band center the more reactive the metal is. The antibonding orbitals become depopulated.
Special adsorption sites

Some examples of the “normal” adsorption sites:

(111) surface
(100) surface
The special sites

A special site is a particularly reactive site

★ at stepped surface
★ at the metal oxide interface boundary for oxide supported
★ at the flat surface of thin metal films
★ at the perimeter of oxide island grown on metal surface
★ etc

Surface steps

Single crystal metal always have atomic steps due to entropic or kinetic reasons.

$N_2$ dissociation flat and stepped Ru:

Both geometric and electronic effect

*S. Dahl et al. PRL vol. 83, 1814 (1999)*
Steps do everything

Au decorates steps:

A reaction site at the perimeter of the metal-oxide interface

Some Au-MgO interface perimeter sites together with a reaction intermediate $[\text{CO} \cdot \text{O}_2]$.

Quasi 1D structures on TiO$_2$ and CO and O$_2$

S.N. Rashkeev et al. PRB, 76, 035438 (2007)

Au adsorption on a thin MgO film supported by Mo

Charged Au Clusters on Metal-Supported Oxides

$\text{O}_2/\text{Au}_1$, $\text{O}_2/\text{Au}_2$, $\text{O}_2/\text{Au}_3$, $\text{O}_2/\text{Au}_4$, $\text{O}_2/\text{Au}_5$, $\text{O}_2/\text{Au}_6$

P. Frondelius et al.
Thin metal films

B. Hammer Topics in Cat. vol 37, 3, (2007)
Pd(111) and Pd(211) surfaces with subsurface carbon

\[ \text{E}_{\text{ads},C} = \frac{E(Pd_s+nC) - E(Pd_s) - nE(C)}{n} \]

\begin{tabular}{c c c c c c}
\hline
Path & Energies (eV) \\
\hline
# & From & To & Barrier & \( \Delta E \) \\
\hline
1 & Fcc & Oct & 0.07 & -0.57 \\
2 & Hcp & Oct & 0.07 & -0.59 \\
3 & Hcp & Tet & 0.40 & 0.01 \\
4 & Hcp & Ffh & 0.12 & -0.75 \\
5 & Ffh & Oct & 0.68 & 0.12 \\
6 & Oct & Oct & 0.66 & 0.20 \\
7 & Oct & Oct & 1.42 & 0.12 \\
8 & Ffh & Oct & 0.98 & 0.33 \\
\hline
\end{tabular}

\[ \text{E}_{\text{ads},C} = \frac{E(Pd_{111}+nC) - E(Pd_{111}) - nE(C)}{n} \]
Mind the gaps!

The issue of lateral interactions (coverage) and how these affect kinetics is of great relevance in so-called “Bridging the Gap” strategies that attempt to translate results obtained from surface science experiments to the situation in an industrial reactor.

Pressure (temperature) gap: low pressure (temperature) or UHV measurement and zero pressure (temperature) DFT calculations versus high pressure (temperature) industrial processes.
Lateral interactions between adsorbates

Adsorbate interactions occur in four classes:

- Direct interactions
- Substrate-mediated interactions
- Elastic interactions
- Nonlocal electrostatic interactions

All interactions display some type of distance dependence and are important at high adsorbate coverage.
CO adsorption over Ru(0001)

Adsorption becomes weaker with increasing coverage.

Adsorption structure affects to adsorption energies.

Different $\text{N}_2$ transition state geometries on stepped Ru
A proper analysis of how the reactivity of an adsorbate changes when neighbors surround it requires that the local environment of each reacting molecule be taken into account separately.

The mean-field approximation is no longer useful!
Ammonia synthesis over Ru


No coverage effects included!!
Compensation effect

\[ r(T) = Ae^{-\frac{E_{\text{app}}}{k_B T}} \]

where

\[ E_{\text{app}} \equiv RT^2 \frac{\partial \ln r_{\text{forward}}}{\partial T} \]

\( E_{\text{app}} \) is the overall activation energy and a composite property of several reaction steps.

Compensation effect: \[ \ln(A) = aE_{\text{app}} + b \]

Experimental observation !

Hydrogenation of of benzene to cyclohexane on Pt(111) and Pt(100). Open symbols refer to Pt(100) and closed ones to Pt(111).

Explanations

- Inherit uncertainties
- A distribution of active sites
- Selective Energy Transfer Model
- A switching of kinetic regimes
Compensation effect


Experimentally measured apparent activation energies and prefactors for NH$_3$ synthesis

Calculated activation energies for N$_2$ dissociation over various transition metals.

The compensation effect in the rate is closely linked to the underlying BEP relationship.
Is there a Compensation effect for NH$_3$ synthesis?

\[
\ln(A) = aE_{app} + b
\]

\[
E_{app} \equiv RT^2 \frac{\partial \ln r_{\text{forward}}}{\partial T}
\]

\[
r(T) = Ae^{-E_{app}/k_BT}
\]
Compensation Effect for a simple kinetic model

reaction 1 \[ A_2 + 2* \rightarrow 2A* \] rate-limiting
reaction 2 \[ A* + B \rightarrow AB + * \] equilibrium

Rate of the total reaction:

\[ r(T, P_x) = 2k_1 P_{A_2} \theta_*^2 (1 - \gamma) \]

\[ \gamma = 1 - \frac{P_{AB}^2}{K_{eq} P_{A_2} P_{B_2}^3} \]

Harmonic transition \[ K_1 = e^{\Delta S_1/k_B} e^{-\Delta E_1/k_BT} - E_a/k_BT \]

The coverage of free sites is

\[ \theta_* = \frac{1}{1 + \sqrt{K_1 P_{A_2} \gamma}} \]

where \[ K_1 = e^{\Delta S_1/k_B} e^{-\Delta E_1/k_BT} \]

Two parameters describing the catalyst are needed.
Switching of apparent activation energy and prefactor is associated with the change in the coverage in free sites.
Two limiting cases:

\[ \Theta_0 \rightarrow 1 \quad r(T) \sim k_1 \sim \nu e^{-E_a/k_BT} \]

\[ E_{\text{app}} = E_a \quad \text{and} \quad \ln A = \ln \nu \]

\[ \Theta_0 \rightarrow 0 \quad r(T) \sim k_1 \theta_*^2 \sim \nu e^{-E_a/k_BT} \left( \frac{1}{\sqrt{K_1}} \right)^2 \]

\[ \sim \nu e^{-\Delta S_1/k_BT} e^{-(E_a - \Delta E_1)/k_BT} \]

\[ E_{\text{app}} = E_a - \Delta E_1 > E_a \quad \text{and} \quad \ln A = \ln \nu - \Delta S_1 > \ln \nu \]

The change in apparent activation energy and prefactor is thus brought about the same switching in kinetic regime and must therefore be correlated.