Introductory Lecture on Computational Materials Design

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OSAKA UNIVERSITY

OUTLINE

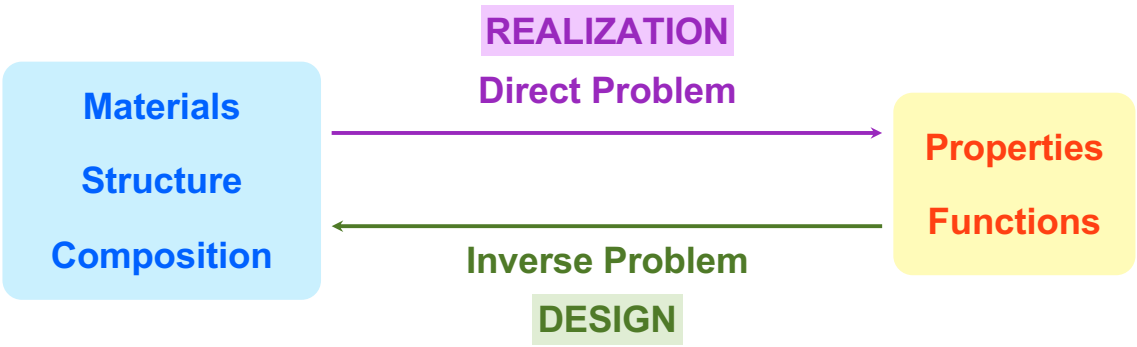
- **Materials Design**
- **Computational Materials Design: CMD®**
- **History of the CMD® Workshop**
- **First-Principles Calculations**
- **Special Features of the Present CMD® Workshop**

CMD® is a registered mark by the CMD® consortium.

Materials Design

- **Goal of Materials Design**
  - **Discovery of novel materials with desired property/function, generally including optimization of property/function that known materials already possess**

- **An Inverse Problem of Realization**



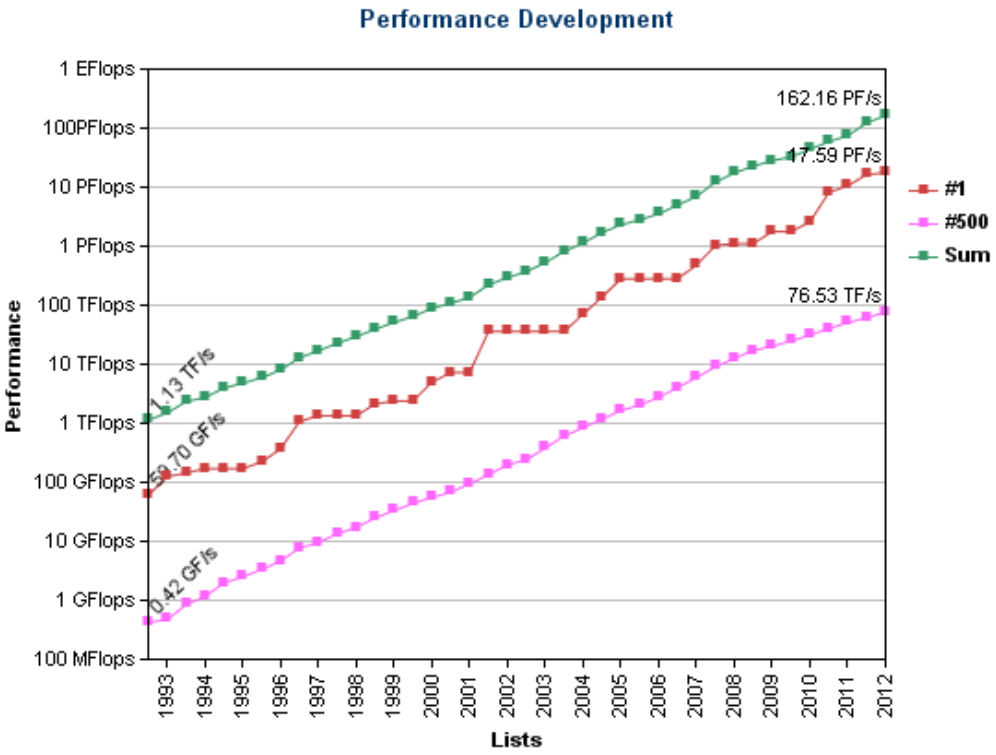
Computational Materials Design: CMD®

- **CMD® is the theoretical design/optimization of materials with desired property/function. Specifically, CMD® involves the efficient use of computational techniques to conduct calculations based on the basic quantum theory.**

- **Key Developments of Emerging CMD®**
  - **Quantum Theory of Electrons**
    - **Electronic states governing most of properties (and often functions) that materials possess**
  - **Computational Techniques: Methods, Algorithms, and Codes**
  - **High-Performance Computers**

- **The purpose of the CMD® Workshop is to provide the fundamental knowledge and techniques needed to enable materials design by computations.**

スーパーコンピューター Top500



Computer exceeds Human Brain?

- Yes in chess in 1997
- Yes in Japanese chess in 2013
- Yes in games of go in 2016.

Computational Materials Design Workshop

- **Background**
  - **In 2001-2002, a Specialist Training Project was held at the International Institute for Advanced Studies (IIAS) in Kyoto, in the field of Information Biology. — An active effort to not merely ensure that the students acquired the target knowledge but rather to create opportunities for bilateral interchange with the instructors, with the aim of using the synergy to train a group of specialists who would become the future leaders in these areas.**
  - **Osaka University had many researchers specializing in first-principles calculations: Profs. H. Akai, H. Katayama-Yoshida, H. Kasai, and so on. They launched the "Development of methods for computational nano-materials design" computer-based project involving some other researchers in Japan under the support of JST in 2001.**
  - **Through the receipt of assistance from the JST project, the CMD® Workshop was born in September 2002 as the second IIAS specialist training project.**

1st CMD® Workshop at IIAS in September 2002

⇧ Morikawa ⇧ Yoshida ⇧ Akai ⇧ Kasai ⇧ Hamada ⇧ Nakanishi

Computational Materials Design Workshop

- Since 2002 the 5-day Workshops have been held twice a year (spring and autumn) and the 33rd Workshop is being witnessed here.
  - Total number of participants (till 32nd WS): 1418
    - Grad. & Undergrad. Students: 815
    - University/College Staffs (incl. National Labs): 248
    - Industry Researchers: 355

http://phoenix.mp.es.osaka-u.ac.jp/CMD/

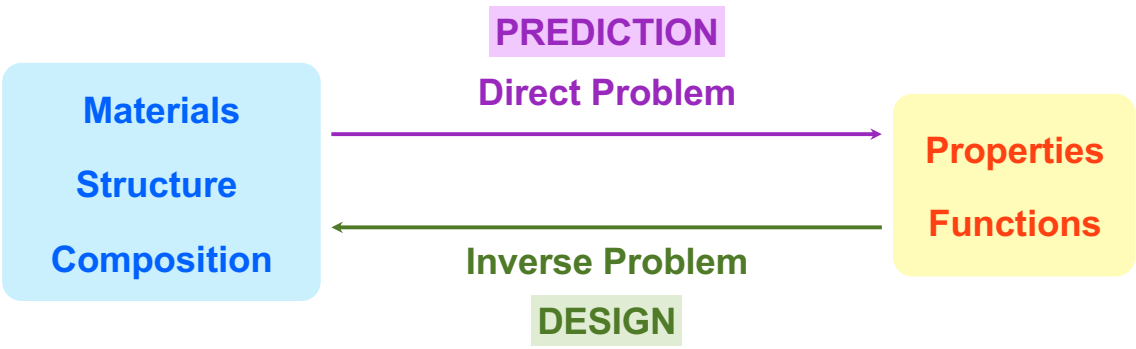
Asian CMD® Workshop

- Since around 2007, the number of foreigners attending the Workshop from Southeast Asia has increased. Most of these are graduate students studying abroad at Osaka University. This made it difficult to conduct the lectures and hands-on training in Japanese only, and not only the explanatory slides but the oral explanations came to be presented in both Japanese and English. This style of instruction has continued to these days, but it has produced problems as well.
- Interchange with people from the Southeast Asian region through the CMD® Workshop became the inspiration in 2008 for the start of Asian CMD® Workshop in Southeast Asia. In August 2008, the first Asian CMD® Workshop was held at Institut Teknologi Bandung in Indonesia. In September 2008, an Asian CMD® Workshop was held at De La Salle University in the Philippines. In the following year, Asian CMD® Workshops were held again in Indonesia and the Philippines, and in Vietnam as well. In 2010, the number of countries was expanded to four with the addition of Thailand. It has continued to be held till these days.

4th CMD® Workshop at DLSU in 2011

First-Principles Calculations

- **Provide a way for solving a direct problem by prediction.**



First-Principles Calculations

★ ***Starting from first principles, equations are derived under some approximations and solved for a realistic system.***

★ ***Two main characteristics:***

- ***General-purpose*: the methods do not depend on material systems and properties to be studied**
- ***Non-empirical*: the methods do not require any experimental parameters and knowledges as input except for fundamental physical quantities (*m*, *e*, *h*)**

  - **We may possibly:**

    Predict properties to be compared with experiments

    Understand underlying microscopic mechanisms

    Design new materials with desired property/function

First-Principles Calculations

- **Basic Approximations**
  - **Born-Oppenheimer Approx. → Interacting N-electron problem under external field (nuclear position: structure)**
  - **One-electron Approx. → Non-interacting problem**
    - **Local Density Approximation to Density Functional Theory**

      Kohn-Sham equations to be solved

- **Band Theory for Crystalline Systems**
- **Real-Space Methods for Nanostructure Systems**

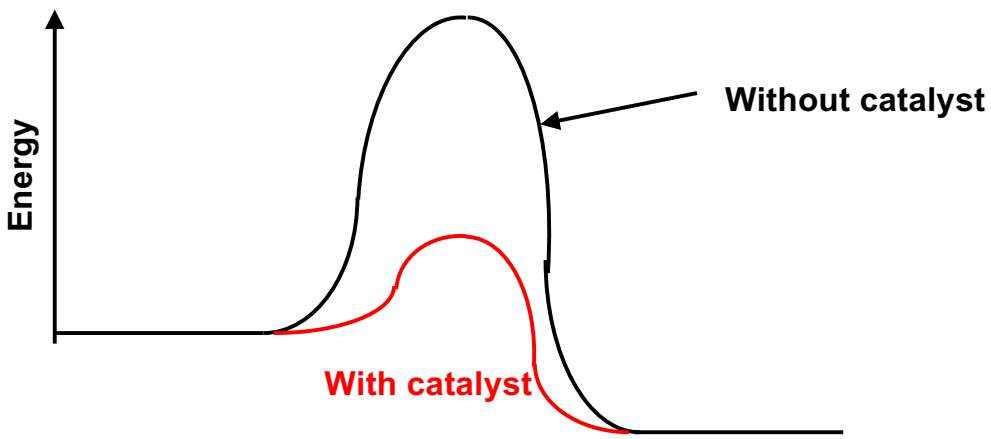
What We Get

- **Many kinds of physical quantities that can be directly compared with experimental observables**
  - ***Structural properties***
    - **heat of formation, phonon, elastic constants, thermal expansion, ...**
  - ***Electric properties***
    - **electric polarization, piezoelectric constants, Born charges, ...**
  - ***Magnetic properties***
    - **magnetic moments (spin and orbital), magnetic coupling, magnetoanisotropy energy, hyperfine constants, ...**
  - ***Optical properties***
    - **optical constants, absorption spectra, ...**
  - **.....**

Catalysis

- Catalyst accelerate chemical reactions by reducing activation barriers but it itself does not change before and after chemical reactions.

A + B → AB



Ammonia synthesis

Fritz Haber
The Nobel Prize in Chemistry 1918

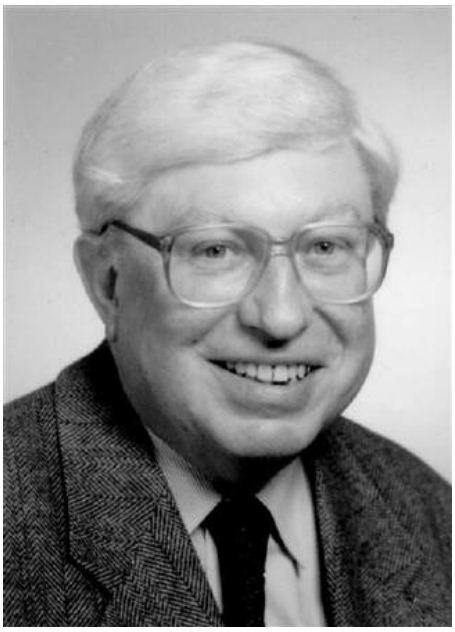
Carl Bosch
The Nobel Prize in Chemistry 1931

- Haber–Bosch process

$$N_2 + 3H_2 \Leftrightarrow NH_3 + 46.1\ kJ/mol$$

- Iron promoted with K_2O and Al_2O_3 ($Fe_3O_4 \cdot Al_2O_3 \cdot K_2O$)
- First manufactured using the Haber process on an industrial scale in 1913 in Germany
- → 80% Fertilizer, plastics, fibers, explosives

Nobel Prize 2007: Gerhard Ertl

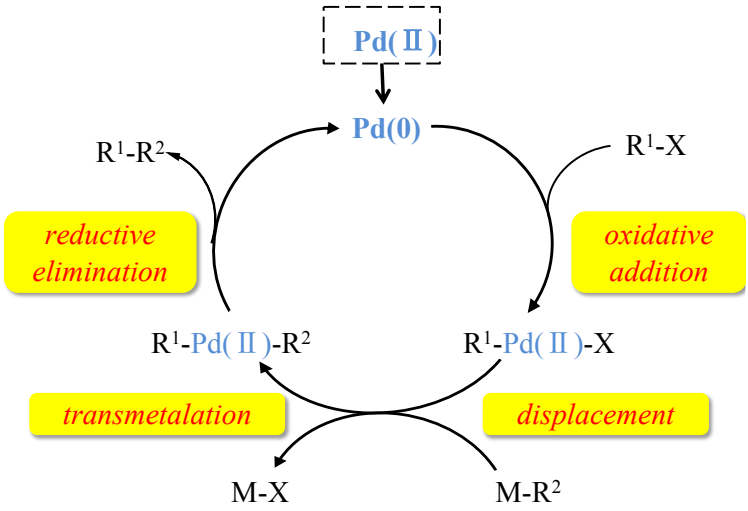


Gerhard Ertl
The Nobel Prize in Chemistry 2007

- Contribution to Surface Chemistry
- Elucidate chemical reactions at solid surfaces in atomic level.

Suzuki-Miyaura cross coupling

Phenylboronic acid + Bromobenzene→Biphenyl



R^1,R^2 = 芳香族化合物
X = ハロゲン

- Important in synthesizing molecules for liquid crystal display, organic electro-luminescent devices, and drugs.

Three way catalyst for Automobil Exhaust Gas

- Convert the following three emission gases.

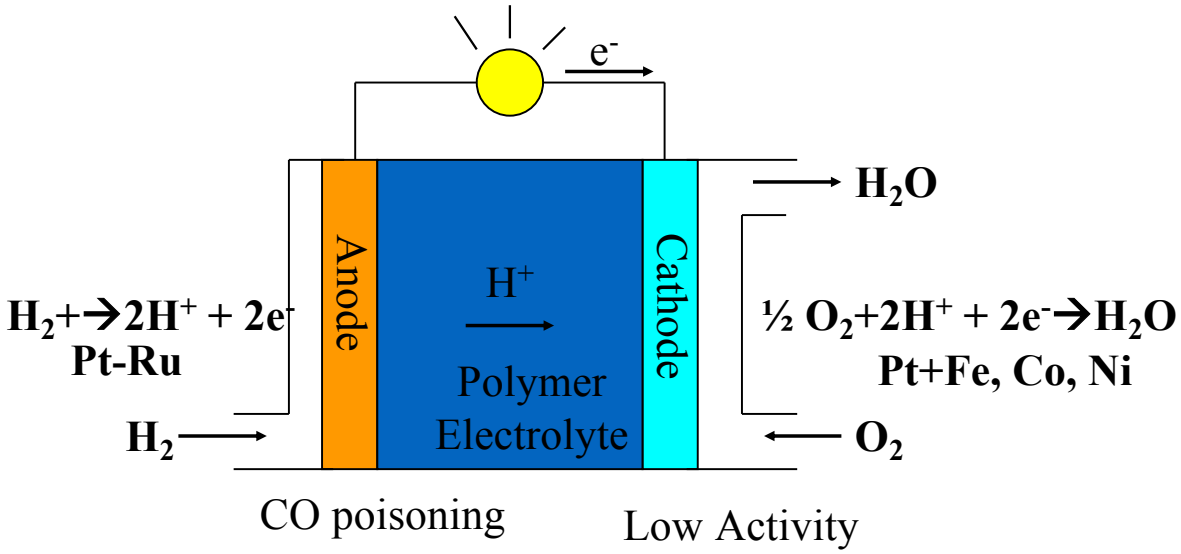
  $CO + O_2 \rightarrow CO_2$

  $NO + CO \rightarrow CO_2 + N_2$

  $HC + O_2 \rightarrow CO_2 + H_2O$
- 三元触媒（Three Way Catalyst）
- Pt･Rh(10:1)、Pt･Pd･Rh、 Pd･Rh、 Pdなど
- Rhは資源的に厳しい。
- Pt: South Africa 74%、Russia 14%
- Pd: South Africa 25% Russia 70%
- Rh: South Africa 67%、Russia 17%

Fuel Cell

Polymer Electrolyte Membrane Fuel Cell



反応の触媒金属依存性

Catalysis

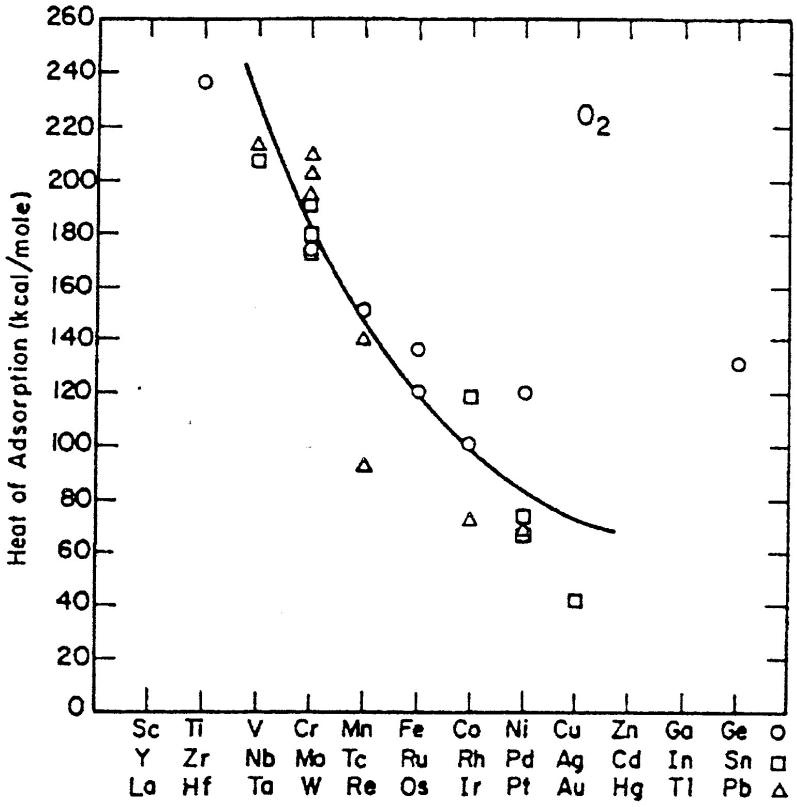
- Catalysts are important in not only industries but also in energy problems and environmental problems.

→ It is necessary to design catalysts with abundant elements.

→ By elucidating reaction mechanisms, it will be possible to design new catalysts theoretically.

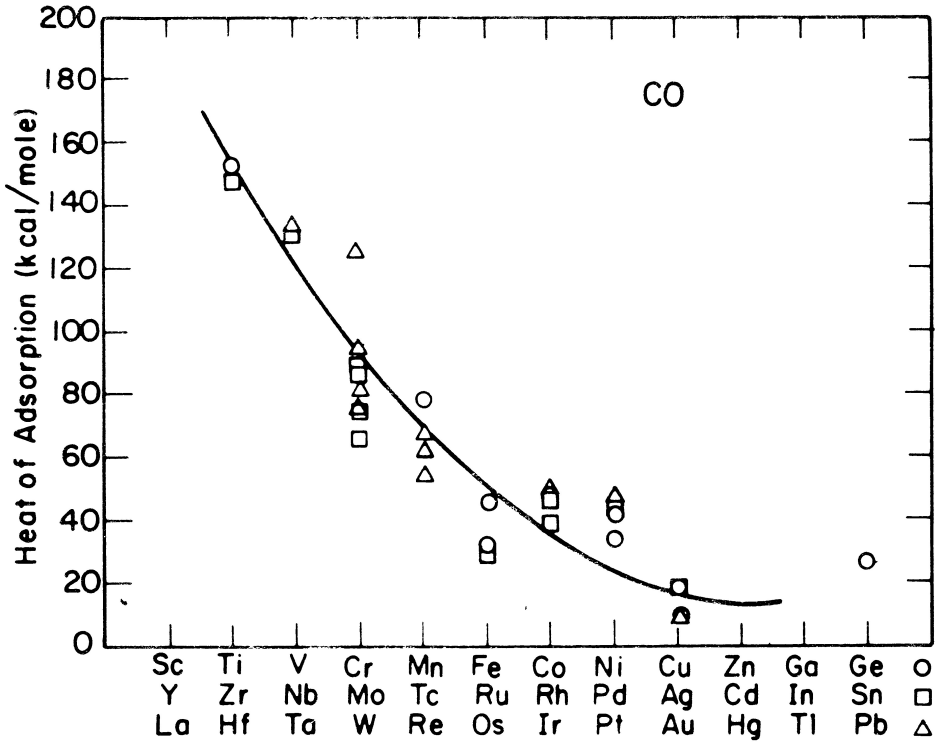
It is possible to clarify mechanisms of chemical reactions from first-principles simulations.

O_2 Adsorption Energy: Substrate metal dependence



I. Toyoshima and G.A. Somorjai, Catal. Rev. Sci. Eng. **19**, 105 (1979).

CO Adsorption Energy: Substrate metal dependence



CO Adsorption State: Substrate metal dependence

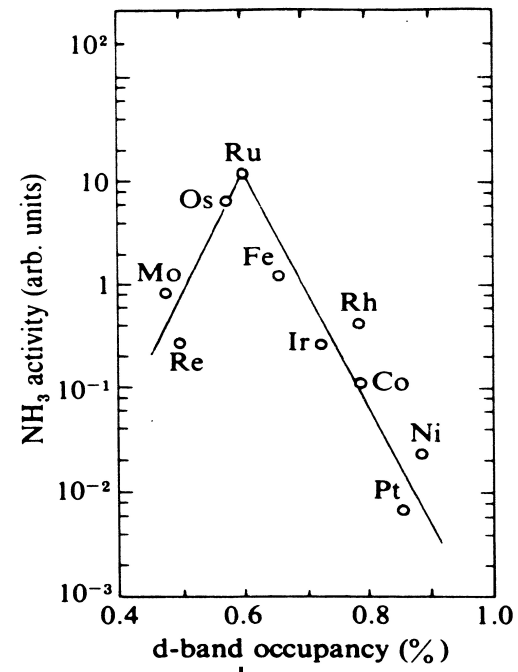
CO

IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB
Sc	Ti D	V	Cr	Mn	Fe D	Co	Ni M	Cu
Y	Zr	Nb	Mo D	Tc	Ru M	Rh	Pd M	Ag
La	Hf	Ta	W D,M	Re	Os	Ir M	Pt M	Au

Dissociate | **Molecular**

G. Borden, T.N. Rhodin, C. Brukner, R. Benbow, and Z. Hurysh, Surf. Sci. **59**, 593 (1976).

Catalytic Activity: Metal dependence

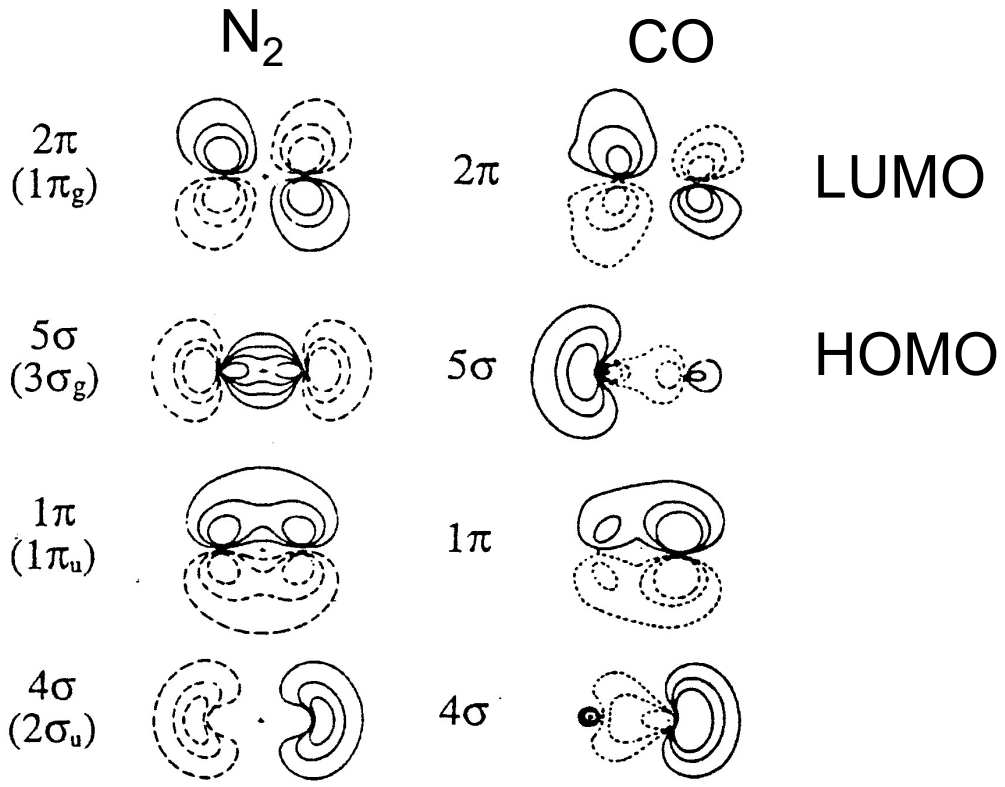


N_2Desorption Limited | **N_2Dissociation Limited**

$$N_2 + 3H_2 \rightarrow 2NH_3$$

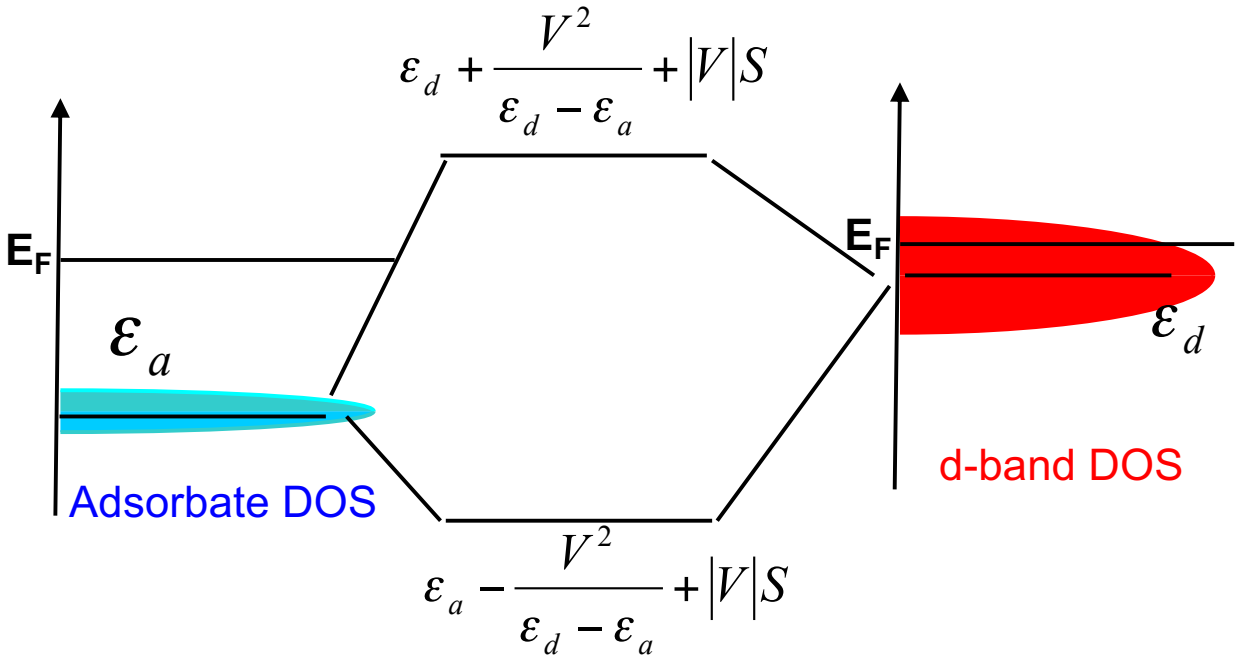
$$N_2 + 2^* \rightarrow 2N_{(a)}$$
$$H_2 + 2^* \rightarrow 2H_{(a)}$$
$$N_{(a)} + 3H_{(a)} \rightarrow NH_{3(a)}$$
$$NH_{3(a)} \rightarrow NH_3\uparrow$$

CO、N_2 Molecular Orbital

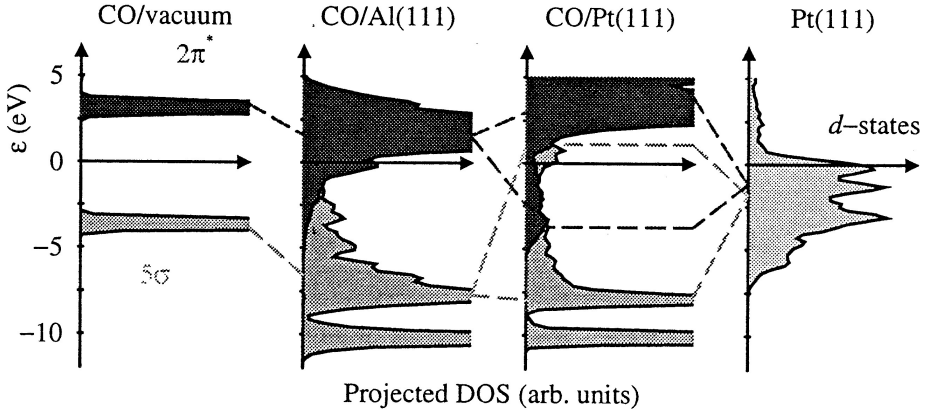


Interaction between MO and d-orbitals

- Second order perturbation



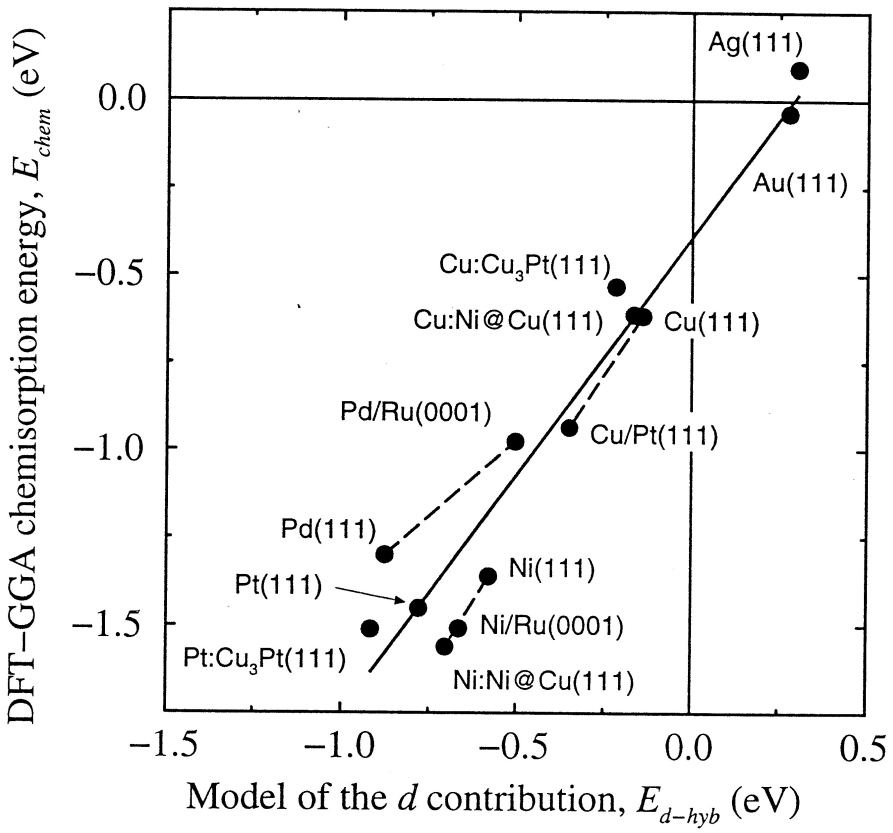
CO adsorption energy



$$E_{d-hyb} \approx -4\left[f\frac{V_\pi^2}{\varepsilon_{2\pi}-\varepsilon_d} - fS_\pi|V_\pi|\right] - 2\left[(1-f)\frac{V_\sigma^2}{\varepsilon_d-\varepsilon_\sigma} - (1+f)S_\sigma|V_\sigma|\right]$$

B. Hammer, Y. Morikawa, J.K. Norskov, Phys. Rev. Lett., **76**, 2141 (1996).

CO adsorption energy



B. Hammer, Y. Morikawa, J.K. Norskov, Phys. Rev. Lett., **76**, 2141 (1996).

Molecular adsorption energy

$$E_{d-hyb} \approx -4\left[f\frac{V_\pi^2}{\varepsilon_{2\pi}-\varepsilon_d} + fS_\pi |V_\pi| \right]$$

$$-2\left[(1-f)\frac{V_\sigma^2}{\varepsilon_d-\varepsilon_\sigma} + (1+f)S_\sigma |V_\sigma| \right].$$

For late transition metals $(f \approx 1)$,

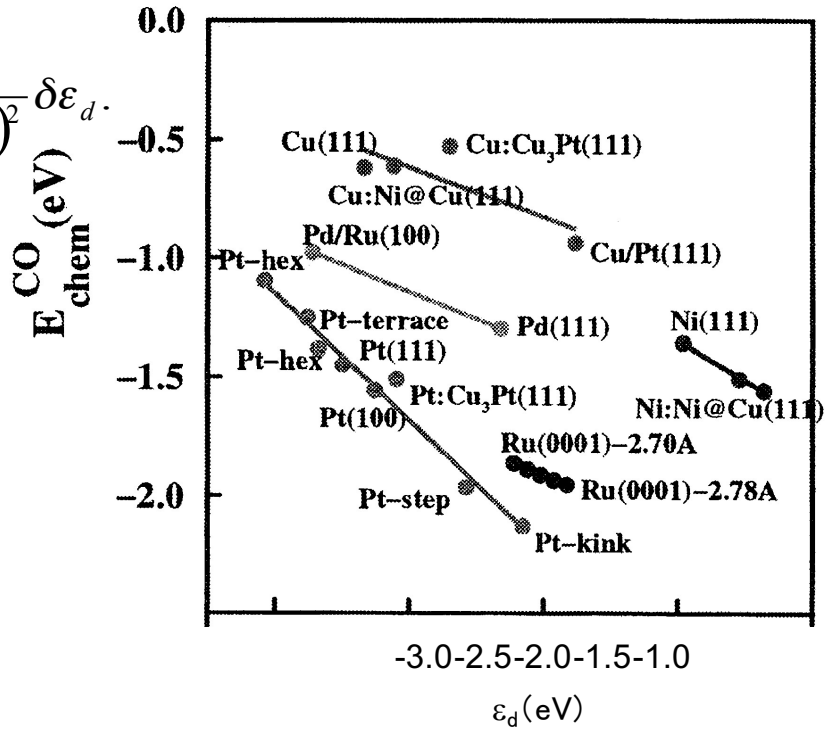
$$E_{d-hyb} \approx -4\left[f\frac{V_\pi^2}{\varepsilon_{2\pi}-\varepsilon_d} + fS_\pi |V_\pi| \right],$$

$$\delta E_{d-hyb} \approx -4f\frac{V_\pi^2}{(\varepsilon_{2\pi}-\varepsilon_d)^2}\delta\varepsilon_d .$$

Adsorption energy VS d-band center

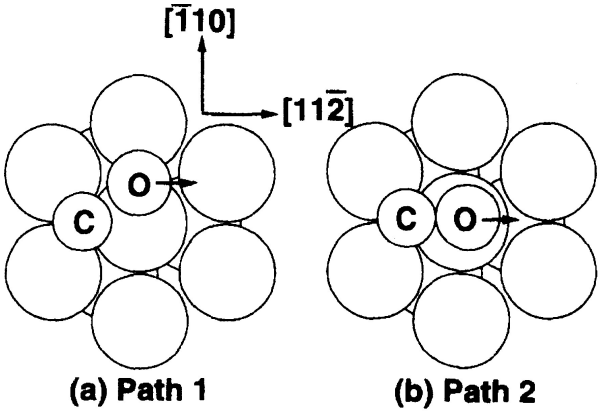
If V is fixed and ε_d is varied

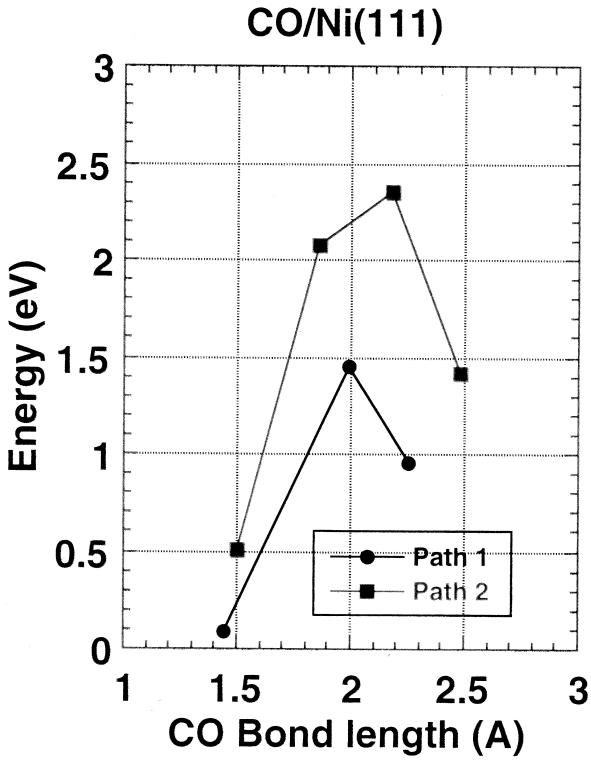
$$\delta E_{d-hyb} \approx -4f\frac{V_\pi^2}{(\varepsilon_{2\pi}-\varepsilon_d)^2}\delta\varepsilon_d .$$



M.Mavrikakis, B. Hammer, J.K. Norskov, Phys. Rev. Lett., **81**, 2819 (1998).

CO dissociation process





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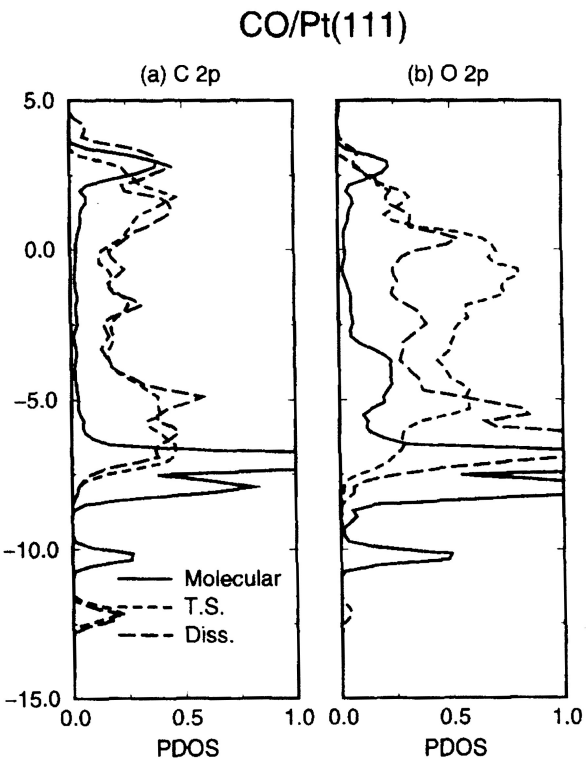
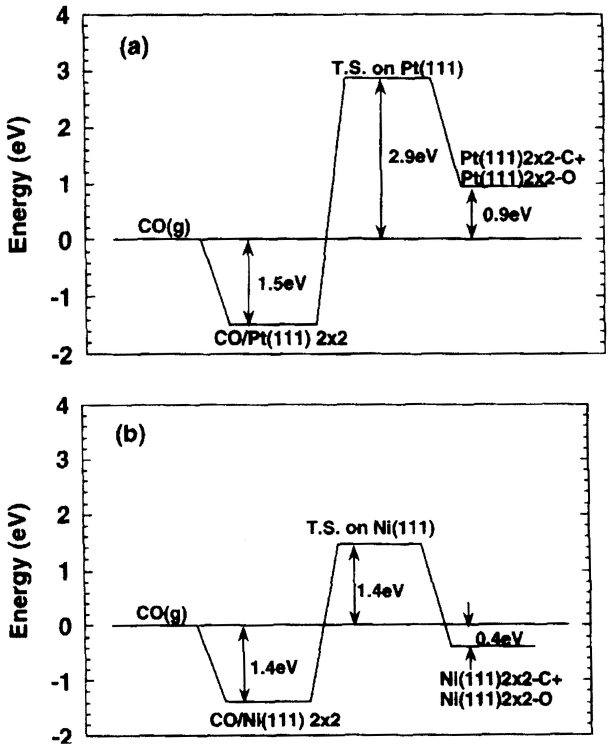
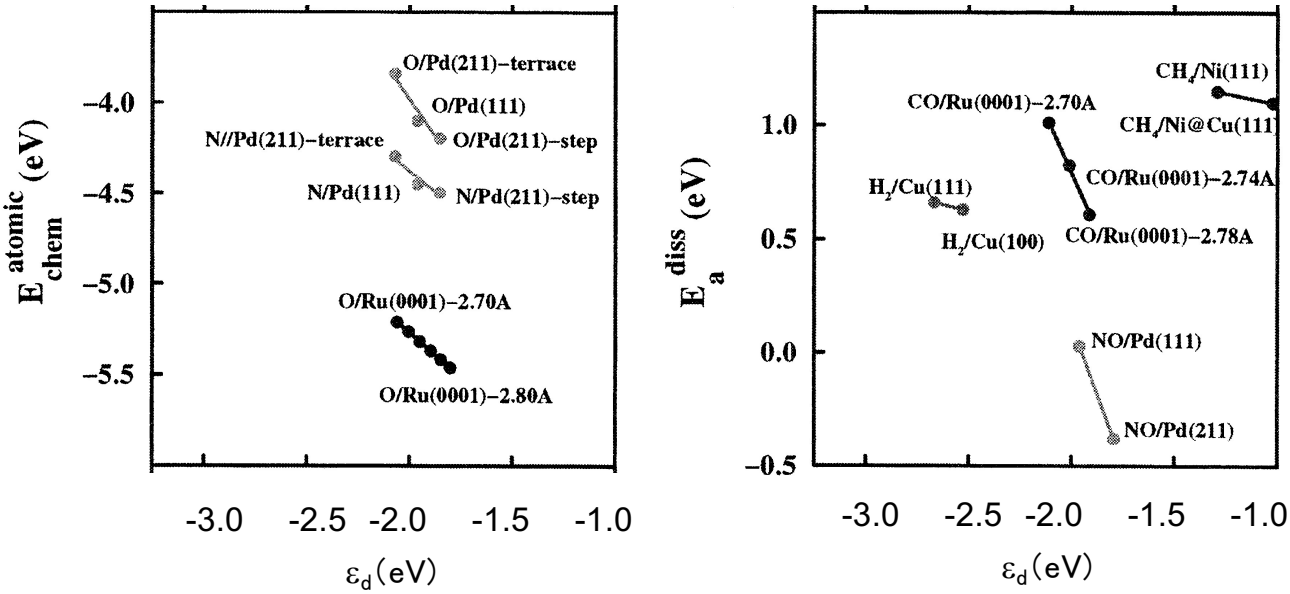




Y.Morikawa, J.J. Mortensen, B. Hammer, J.K. Norskov, Surf. Sci., **386**, 67 (1997).

Adsorption Energy and d-band center



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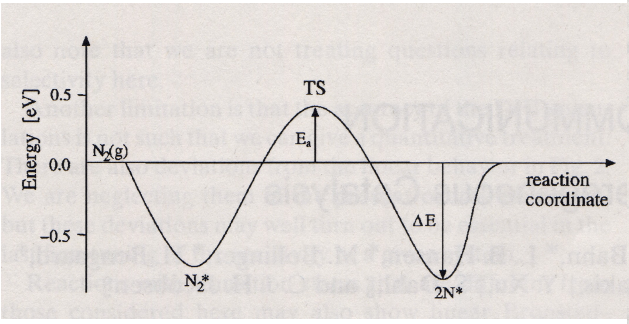
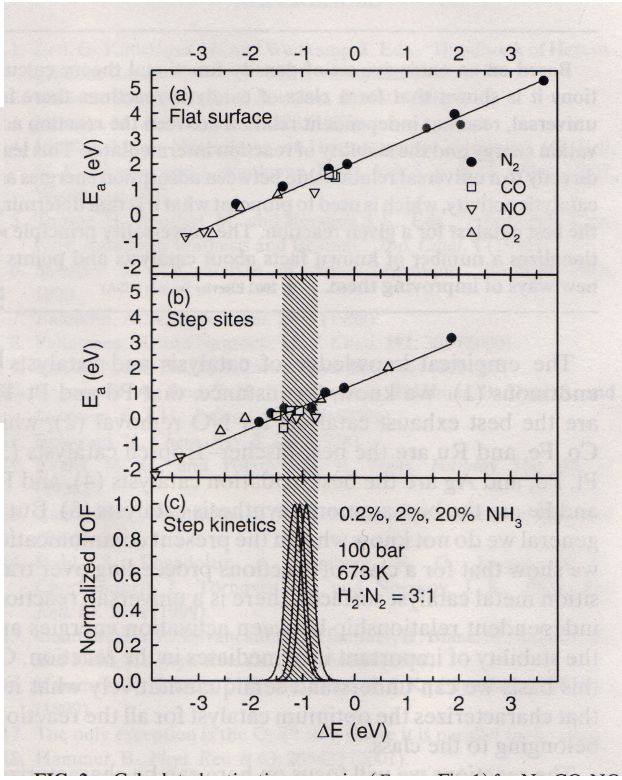
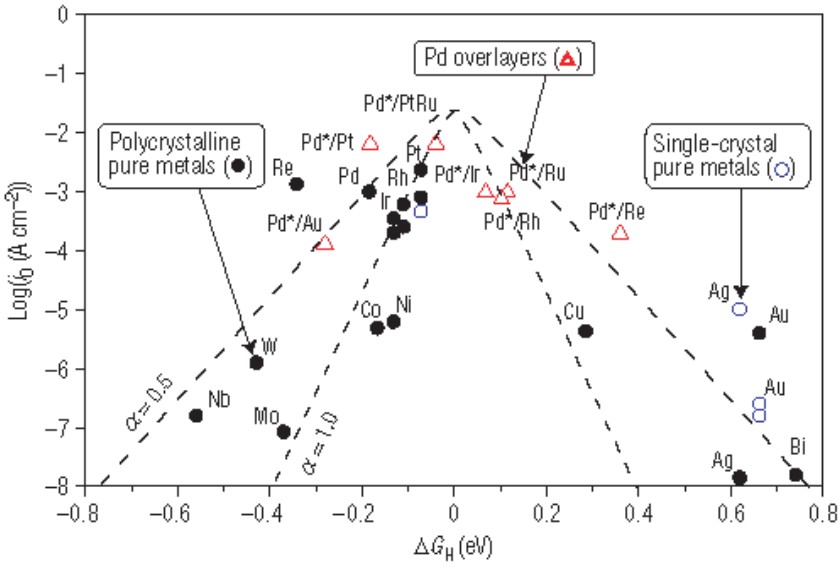
Universality in Heterogeneous Catalysis





J.K. Norskov et al., *J. Catal.* 209, 275 (2002).

Hydrogen Evolution Reaction



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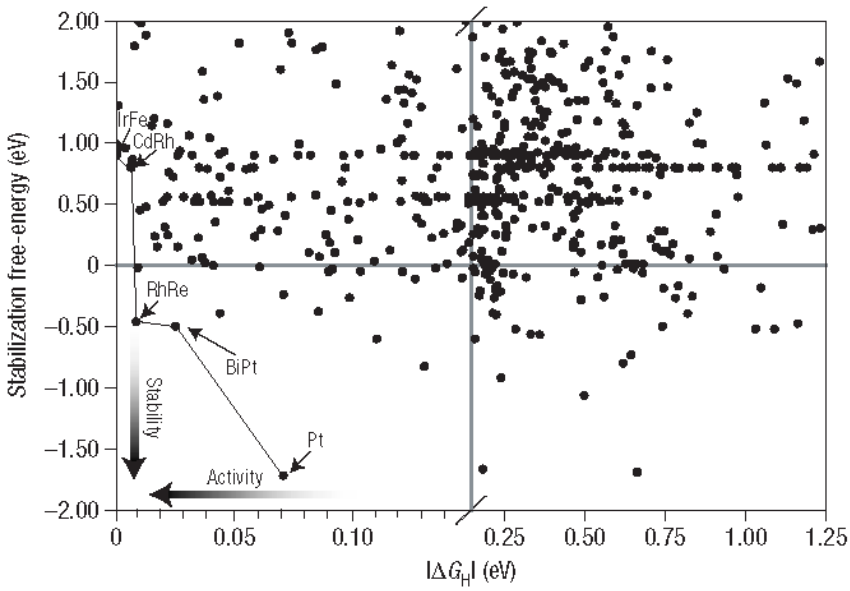

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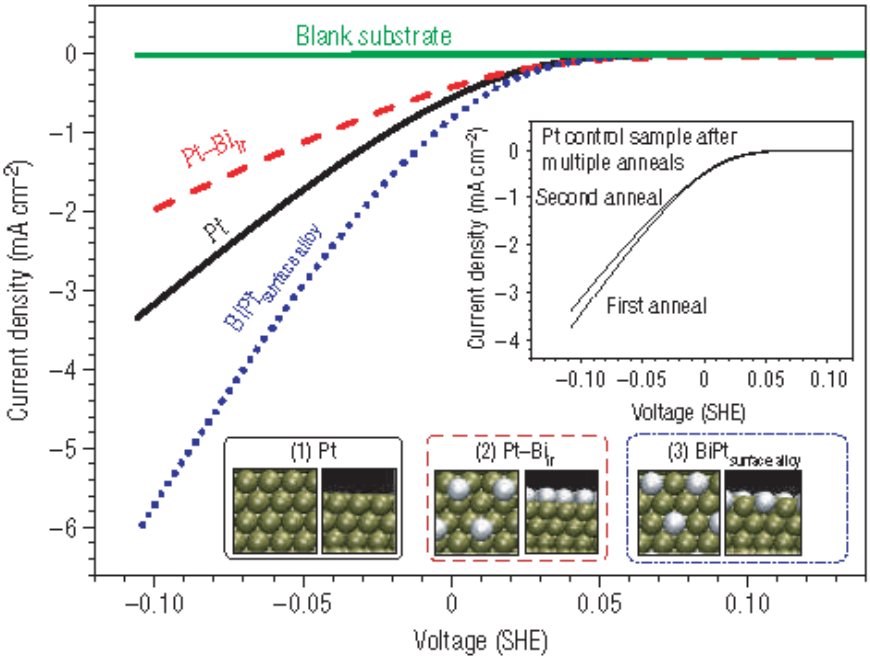

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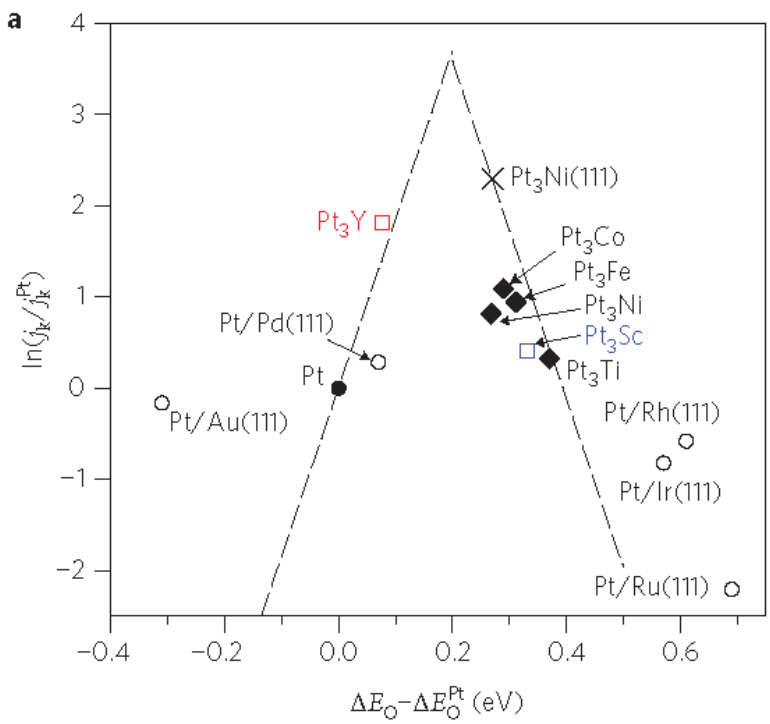
Oxygen Reduction Reaction



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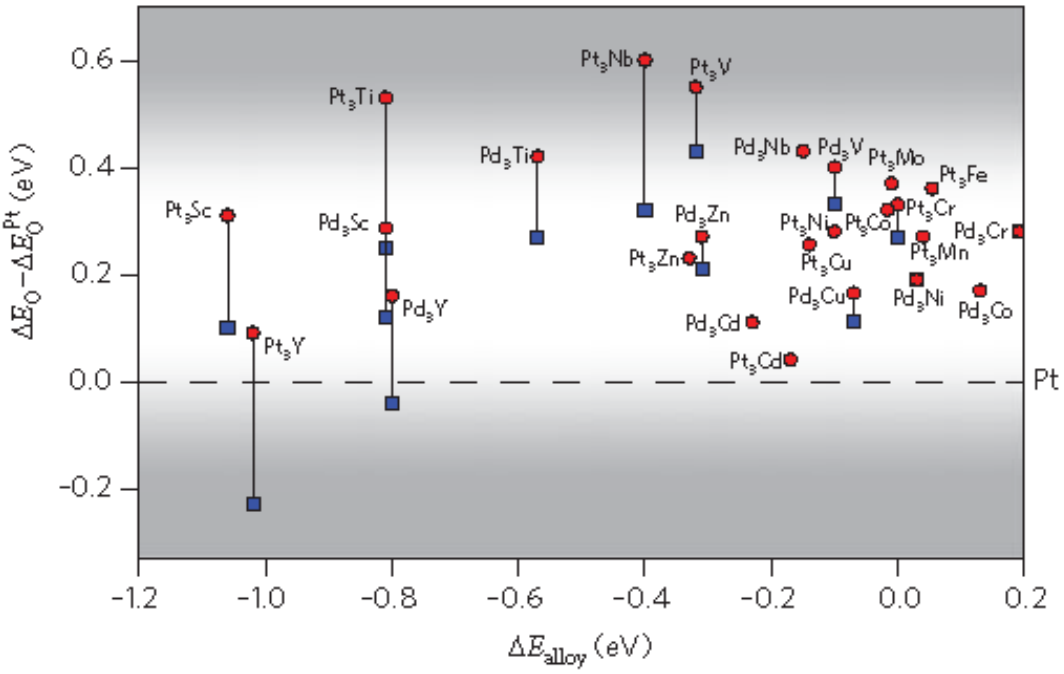

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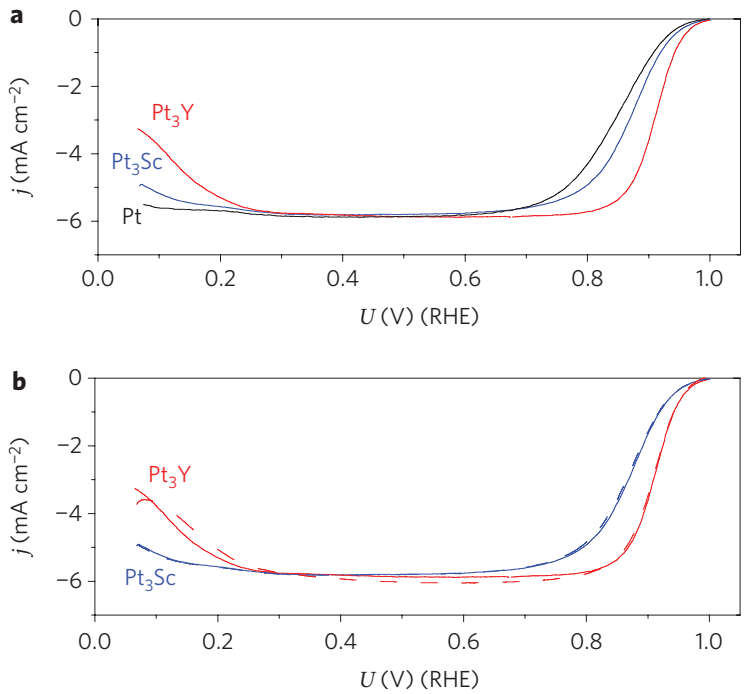

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30th CMD® Workshop

- Beginners Course
  - Machikaneyama, STATE-Senri, ABCAP
- Advanced Course
  - HiLAPW, feram, Machikaneyama, Naniwa, STATE-Senri
- Supercomputer Course
  - RSPACE
- Expert Course
- Spintronics Design Course
- Lectures
  - Case Study I–IV
  - Special Lecture I-II

Hope you enjoy the Workshop

http://phoenix.mp.es.osaka-u.ac.jp/CMD/