First Principles Multiscale Modelling to design Pt-based bimetallic catalysts for (de)hydrogenation reactions

Marie-Françoise Reyniers, Maarten K. Sabbe and Guy B. Marin

Laboratory for Chemical Technology
Metal catalyzed processes


Conversion, %
Temperature, K

1 MPa
2 MPa
3 MPa

microscopic
nm
active center

introduction
approach
challenges
case benzene
case propane
take home
Metal catalyst design: goal

Find best trade-offs by optimizing:

- catalyst composition
- reaction conditions:
  - pressure
  - temperature

Conflicting objectives

identification of Pareto optimal solutions
Metal catalyst design: approach

- Catalyst composition & structure
- Electronic structure
- Reactivity & selectivity

Density of states (eV\(^{-1}\))

Energy \((E-E_f)\)

Conversion, %

Temperature, K

1 MPa

2 MPa

3 MPa
First principles based multiscale modelling of catalytic processes

- electronic structure (0 K)
- vibrational analysis
- statistical thermodynamics
- H(T), S(T), G(T)
- thermo & kinetics $K, k_+, k_-$
- reactor hydrodynamics
- mass/heat transport
  - surface coverages
  - rate analysis
  - operative mechanism
  - conversion & product yields

$E(0K) = f(\text{catalyst descriptor})$

Guidelines for optimal catalyst properties & reaction conditions
Use d-band property as catalyst descriptor

Density of states (eV$^{-1}$)

- DOS at Fermi level
- Center of occupied d-band

<table>
<thead>
<tr>
<th>No</th>
<th>Descriptor</th>
<th>Symbol</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>d-band center of the whole d-band relative to the Fermi level</td>
<td>$\varepsilon_d - E_{Fermi}$</td>
<td>[eV]</td>
</tr>
<tr>
<td>2</td>
<td>d-band center of the filled d-band relative to the Fermi level</td>
<td>$[\varepsilon_d - E_{Fermi}]_{\text{filled}}$</td>
<td>[eV]</td>
</tr>
<tr>
<td>3</td>
<td>Density Of States at the Fermi level of the total DOS</td>
<td>$DOS_{Fermi}$</td>
<td>[-]</td>
</tr>
<tr>
<td>4</td>
<td>Density Of States at the Fermi level of the d-band DOS</td>
<td>$[DOS_{Fermi}]_{d\text{-band}}$</td>
<td>[-]</td>
</tr>
<tr>
<td>5</td>
<td>Width of the d-band at quarter height</td>
<td>$W_{d,\text{quarter}}$</td>
<td>[eV]</td>
</tr>
<tr>
<td>6</td>
<td>Width of the d-band at half height</td>
<td>$W_{d,\text{half}}$</td>
<td>[eV]</td>
</tr>
<tr>
<td>7</td>
<td>Carbon adsorption energy on hcp-M site</td>
<td>$\Delta E_{\text{ads, C}}$</td>
<td>[kJ mol$^{-1}$]</td>
</tr>
<tr>
<td>8</td>
<td>Interaction energy between the alloy and adsorbed carbon</td>
<td>$\Delta E_{\text{interaction, C}}$</td>
<td>[kJ mol$^{-1}$]</td>
</tr>
<tr>
<td>9</td>
<td>Antisegregation energy</td>
<td>$\Delta E_{\text{antisegr.}}$</td>
<td>[eV]</td>
</tr>
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</table>
Catalyst descriptor: principle

Pt$_3$M alloys (111); M = Ag, Au, Cu, Fe, Co, Ni, Pd

Pt$_3$M
- bulk alloy
- segregated

Pt$_3$M/Pt
- surface alloy
- anti-segregated

Pt$_3$M alloys (111); M = Ag, Au, Cu, Fe, Co, Ni, Pd

- most stable alloy
- most stable benzene adsorption site
- $E_a$ first H-addition

E$_{ads}$ (kJ/mol)

$\varepsilon_d - E_f$

$\varepsilon_d - E_f$

center occupied $d$-band
Challenges FP-modeling catalytic reactions

- electronic structure (0 K)
- vibrational analysis
- statistical thermodynamics

- H(T), S(T), G(T)

- thermo & kinetics
  - K, k+, k−

- E(0K)

Introduction  Approach  Challenges  Case benzene  Case propane  Take home
Typical challenges: 1. the “active site”

• The “active site” as defined in *IUPAC Gold Book*
  “The term is often applied to those sites for adsorption which are the effective sites for a particular heterogeneous catalytic reaction.”

• The “active site” as frequently used in kinetic modeling
  • a single type of site
  • uniformly distributed over the surface
  • represented by ★

• The “active site” as required for first principles calculations
  • a precisely formulated, atom-defined entity:
    • well-defined surface structure
    • well-defined site geometry (xyz coordinates)
    • multiple catalyst-adsorbate bonding patterns
    • precise amounts of dopants, additives, adatoms
    • particular edge and support effects

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Bimetallics: the “active site”

1st approximation

Bimetallic catalyst particle

(100) facet

(111) facet

2nd approximation

‘skin’ or ‘monolayer’ models

‘surface sandwich’ models
Typical challenges: 2. computational method

Jacob’s ladder illustrates DFT functional hierarchy

- Increasing complexity and computational requirements

**RPA**
- 5th: ?
- “advanced”

**“Non-empirical” (constraint satisfaction)**
- 4th: hybrids
- (gas phase standard)

**PBE**
- 3rd: meta-GGA

**“Empirical” (property satisfaction)**
- 2nd: GGA
- 1st: LDA

**DFT-D**
- 5th: ?
- “advanced”

PBE is the common workhorse for heterogeneous catalysis
- no van der Waals interactions
- generic uncertainty of 20-30 kJ/mol through error cancellation

‘semi-empirical’ DFT-D methods
- fast: negligible computational cost
- parameterized ⇒ manifold of methods
- performs well for molecular and band gap systems
- problematic for interaction with metal surfaces

RPA is the ‘best’ tool for heterogeneous catalysis
- but computationally out of reach
Typical challenges: 3. coverage dependence

Experimental data shows that adsorption enthalpies are strongly coverage dependent.

**Benzene adsorption energy** $\Delta_{\text{ads}} H(B)(\theta_B)$

- $\Delta_{\text{ads}} H(B)(\theta_B) = (197 - 48 \cdot \theta - 83 \cdot \theta^2) \text{ kJ/mol}$

**$H_2$ adsorption energy** $\Delta_{\text{ads}} H(H_2)(\theta_B)$ (differential)


- 300 K, Pt/SiO$_2$ (low and high dispersion), Pt powder, Pt(111) by nuclear and recoil scattering.

Case: benzene hydrogenation on Pt(111)
Kinetics at low coverage: ortho path dominant

rate coefficients $k$ (s$^{-1}$) (450K)

forward reverse

DP$_{\text{cluster}}$
minimum energy path (periodic Pt(111))
PW91 functional

DP based on $\mu$-kinetic simulation

benzene adsorbed at hollow adsorption site: more reactive than bridge (based on $\Delta^\ddagger E_{el}$)
PW91, low coverage: too low TOF’s

**CHA yield parity plot**

- **Dependence of conversion** (2 scales)

- Rates 6-7 orders of magnitude too low
- Incorrect temperature dependence
- Partial reaction orders too high, and wrong sign for benzene

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**Property** | **Experiment** | **Simulated**
--- | --- | ---
Range $R_{CHA}$ (mol/s) | $4 \times 10^{-6} - 5 \times 10^{-5}$ | $7 \times 10^{-13} - 6 \times 10^{-11}$

$n_{H_2}$ ($p_{tot} = 30$ atm, $p_B = 0.6$ atm) | 0.45 - 0.69 | 0.69 - 1.02

$n_B$ ($p_{H_2} = 3$ atm) | $-0.04 - -0.32$ | 0.94 - 1.00
Kinetics at $\theta H = 0.44$: ortho path dominant

13CHD(gas) $\rightarrow$ CHE(gas)

\[ \text{optPBE vdw-DF functional} \]
vdw-DF, $\theta H = 0.44$: good agreement

Cyclohexane product yield

Outliers: 423 K (150 °C)

Temperature dependence of conversion

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<td>$n_{H2}$ ($p_{tot}$ = 30 atm, $p_B$ = 0.6 atm)</td>
<td>0.45 - 0.69</td>
<td>0.49 – 0.64</td>
</tr>
<tr>
<td>$n_B$ ($p_{H2}$ = 3 atm)</td>
<td>$-0.04 - -0.32$</td>
<td>$-0.32 - -1.02$</td>
</tr>
</tbody>
</table>

- Fair agreement to experimental product yields and captures trends
- Correct qualitative behavior of conversion vs. $T$
- Partial reaction orders:
  - For $H_2$ close to experiment
  - For benzene too low
- Selectivity: only CHA if $T > 450K$

Sabbe et al., JCat, 330(2015):406
Can this be further improved?

Temperature dependence of conversion

- underestimation of rate at 30 atm
- overestimation of rate at 10 atm
- underestimation of rate at low T
- conditions corresponding to H coverages $\theta_H > 0.44$?
- conditions corresponding to H coverages $\theta_H < 0.44$?
- is a dynamic, explicit coverage dependence as function of the conditions required?

already evaluated for benzene hydrogenation on Pd(111)
Coupling between microkinetic simulation & coverage-dependent kinetics

Rate coefficients calculated at 4 coverages:

\( \theta_H = 0.11 \), \( \theta_H = 0.11 \), \( \theta_H = 0.44 \), \( \theta_H = 0.67 \)

\( \theta_{tot} = 0.11 \), \( \theta_{tot} = 0.22 \), \( \theta_{tot} = 0.55 \), \( \theta_{tot} = 0.78 \)

Regression of linear relations to kinetic parameters at 4 coverages

For every reaction step:

\[ E_a = a \theta_{tot} + b \]

\[ \Delta^{\ddagger}S = a \theta_{tot} + b \]
Dynamic coverage-dependent kinetics on Pd(111)

**Experiment vs. Simulated Kinetics**

**Table:**

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<tr>
<th>Parameter</th>
<th>Experiment $^a$</th>
<th>Simulated</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{CHA}$ (mol/s)</td>
<td>$6 \times 10^{-3}$ - 1.1</td>
<td>0.2</td>
</tr>
<tr>
<td>$n_B$</td>
<td>-0.5 - -0.2</td>
<td>-0.02</td>
</tr>
<tr>
<td>$n_{H2}$</td>
<td>~1</td>
<td>1.2</td>
</tr>
</tbody>
</table>

*Conditions: 413 K, $p_{H2} = 0.9$ bar, $p_B = 6.6 \times 10^{-2}$ bar*

$^a$ Chou & Vannice J.Cat., 107 (1987):129-139

**Graphs:**

- **Activity well predicted compared to experiment**
  - $T_{max TOF, exp}$
  - Various data points from Chou & Vannice, Vannice & Neikan, Moss et al., etc.

- **Selectivity well predicted for T > 400 K**
  - Cyclohexane and Cyclohexene

- **Total coverages in range 0.5 - 1**
  - $H$ and $B$ fractions vs. $T$ (K)
Benzene hydrogenation: take home

• critical selection of catalyst model, computational method and effects to be included requires benchmarking/feedback from experiment

• accounting for explicit coverage dependence brings quantitative agreement at industrially relevant reactions conditions within reach

\[
\frac{d\theta_i^*}{dt} = R_i^* 
\]

coverage-dependent kinetics
\[ k(\theta_{tot}), K(\theta_{tot}) \]

microkinetic simulation

surface science & catalytic data in broad range of experimental conditions

selection catalyst model & computational method
Case: propane dehydrogenation on Pt/Ga

μ-kinetics: rate analysis on Pt(111)

based on DFT data on Pt(111)

• \( r_1 \) (propane adsorption) ~ ACTIVITY

• \( r_{26} \) (C-C scission) ~ SELECTIVITY

full network contains 41 elementary steps (forward & backward)

Saerens et al., ACS Catal. 2017, 7, 7495−7508
C-C scission on Pt₃Ga vs Pt

High barrier for C-C scission of propyne on Pt₃Ga(111)

→ no formation of ethylidyne and methylidyne

→ negligible formation of side products coke, CH₄, C₂H₆ and C₂H₄
Coke formation on step sites?

- Pt(211) surface → include step sites
- Energetics at relevant reaction step for coke formation:

\[
\begin{align*}
\text{CH}-\text{C}-\text{CH}_3 & \xrightarrow{30 \text{ kJ/mol}} \text{CH}_3\text{-C} + \text{CH} \\
\text{Pt}_2\text{Pt}_2 & \text{propyne} & \equiv & \text{Pt}_3\text{Pt}_3 & \text{ethyldiyne} & \text{methylidyne}
\end{align*}
\]

Pt(111): \( \Delta E_{\text{elec}} = -64 \text{ kJ/mol}, \ E_{a,\text{elec}} = 113 \text{ kJ/mol} \)
Pt(211): \( \Delta E_{\text{elec}} = -53 \text{ kJ/mol}, \ E_{a,\text{elec}} = 96 \text{ kJ/mol} \)

- Selective blocking of defect sites by Ga atoms:

Ga prefers to sit in low-coordinated sites such as edges, kinks and steps:

Ga on surface step → Ga in (111) surface plane 22 kJ/mol

\( \times \) Coke formation via atomic carbon or on step sites less likely for Pt\(_3\)Ga
Pt3M bimetallics

DFT data for all important steps on Pt₃M(111)

- \( r₁ \) (propane adsorption) \( \sim \) ACTIVITY
- \( r₂₆ \) (C-C scission) \( \sim \) SELECTIVITY
Identification of catalyst descriptor: d-block

- correlation & regression analysis of DFT data on all important reaction steps
- d-block alloys: a single descriptor can be used for all reactions; $\Delta E_{ads,C}$ works best

$$\frac{\Delta E_{r,i}}{E_{a,i}} = \alpha_i + \beta_i \cdot \Delta E_{ads,C}$$

**example:** $\Delta E_{ads, \text{reaction 5}} = f(\Delta E_{ads,C})$
µ-kinetic mapping: d-block

- **strong** carbon adsorption
  - ⇒ high activity

- **weak** carbon adsorption
  - ⇒ high selectivity
  - ⇒ good anti-coking ability

\[(T = 600 \, ^\circ C, \, p = 1 \, \text{atm}, \, WHSV = 882 \, \text{h}^{-1})\]
Multi-objective optimization: d-block

optimal trade-offs between catalytic activity, selectivity and anticioking ability = f(descriptor)

\[(T = 600 \, ^\circ C, \, p = 1 \, atm, \, WHSV = 882 \, h^{-1})\]
Multi-objective optimization: d-block catalyst composition & price

trade-off window for

- activity
- selectivity anti-coking ability
- low-priced

Metal M purchase cost [USD mol⁻¹]

ΔE_ads, C [kJ mol⁻¹]
Identification of catalyst descriptors: p-block

- correlation & regression analysis of DFT data on all important reaction steps
- **p-block** alloys: two descriptors needed; $DOS_{\text{Fermi}}$ and $d$-band center
μ-kinetic mapping: p-block

(\(T = 600 \, ^\circ C, \, p = 1 \, \text{atm}, \, WHSV = 882 \, \text{h}^{-1}\))

(\(T = 600 \, ^\circ C, \, p = 1 \, \text{atm}, \, WHSV = 8.82 \, \text{h}^{-1}\))
Multi-objective optimization: p-block

-catalyst composition & price

Metal M purchase cost [USD mol⁻¹]

DOS/Fermi [-]

used industrially

Pt₃Ga
Pt₃Ge
Pt₃In
Pt₃Sn
Pt₃Pb

activity

-2.2 -2.1 -2.0 -1.9 -1.8

εₜ-E_Fermi [eV]

anti-coking ability

used industrially
Multi-objective optimization: p-block

-simultaneous optimization of p and T for Pt$_3$Ga

- at low single pass conversion
  - p > 3 atm
  - T < 600°C
- at higher single pass conversion
  - p < 3 atm
  - T > 600°C
Propane dehydrogenation: take home

Design of bimetallic catalysts can be speeded up by combining:

• first principles based activity-catalyst descriptor relations

• $\mu$-kinetic modelling

• multi-objective optimization

The approach allows defining optimal trade-offs between composition, reaction conditions and catalyst cost allowing to reach predefined ranges of activity, selectivity and coke formation