Predicting the activity of amorphous catalyst sites and supported nanoparticle stability via first-principles

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Catalysis is a multibillion-dollar industry
Towards understanding the synthesis, activity, and stability of catalysts

Modeling quenched disorder of catalyst sites on amorphous supports

Kinetics of homogeneous catalysts

Predicting the stability of supported nanoparticles

Nucleation & growth of nanoparticles

(CH3)2Au(acac)
Applying modeling to understand the synthesis, activity, and stability of catalysts

Modeling quenched disorder of catalyst sites on amorphous supports

Predicting the stability of supported nanoparticles
Catalysis by crystalline materials: from structure to properties

Cluster models

Real system
Model system
Cut, cap and constrain

Slab models

Interface confined ferrous centers

1. British Zeolite Association webpage http://www.bza.org/
2. X. Rozanska et.al., J. Catal., 2002, 388
3. Q. Fu et. al. Science 328, 2010, 1141

$E_{\text{act}} = 318 \text{ kJ/mol}$
Modeling amorphous catalysts has been an intractable problem

- Some catalysts only work on amorphous supports
- Unknown initiation mechanism
- How do typical dead sites and active sites differ?

Cr/SiO$_2$
Cr/AlPO$_4$
CH$_3$ReO$_3$/silica-alumina
Mo/SiO$_2$
Ti/SiO$_2$
Ta/SBA15
Drawings specify topology, but activity also depends on site environment

Ruddy and Tilley, JACS, 130, 11088 (2008)

Chizallet and Raybaud, Angew. Chem. 48, 2891 (2009)
Single atom catalysts on amorphous supports: a quenched disorder perspective

Rate for site geometry $x$

$$k(x) = A(x) \exp[-\beta \Delta E(x)]$$

$$\langle k \rangle = \int dxxk(x)\rho(x)$$

Projected to activation energy distributions

$$\tilde{\rho}(\Delta E) = \int dx\rho(x)\delta[\Delta E - \Delta E(x)]$$

$$k(\Delta E) = \tilde{\rho}(\Delta E)^{-1} \int dx\rho(x)k(x)\delta[\Delta E - \Delta E(x)]$$

$$\langle k \rangle = \int d\Delta E \ k(\Delta E)\tilde{\rho}(\Delta E)$$

Rate-weighted distribution of catalyst sites

$$\tilde{\rho}(\Delta E)$$

Kinetics are highly sensitive to the low energy tail

New methods are needed to sample the most reactive sites

Typical modeling protocols for amorphous materials

Often necessary to make undesirable assumptions

Use an approximate support and model in the gas phase

CH$_3$ReO$_3$ on ‘amorphous silica-alumina’

- Too flexible
- No constraints to mimic solid support

Typical modeling protocols for amorphous materials

Use a crystalline support with rigid constraints

Mo/Silica catalyst cut from β-cristobalite

two out of 10 different models tested

Our approach to modeling isolated catalyst sites on amorphous supports

Modeling premises

1) Periphery atoms ($x_p$) should be immobile

2) Periphery atoms influence chemical properties of the site

3) Periphery atoms arranged in an unknown and continuous distribution

4) For any $\Delta E^\ddagger(x_p)$, assume low energy sites prevalent
Connecting our algorithm to usual zeolite modeling approach

1) $x_p$ should be immobile

2) $x_p$ influence chemical properties

3) continuous $x_p$ distribution

4) low energy site preference

Our Algorithm

Amorphous: What is the best place to put $x_p$?

$$\min_{x_p} E^A_{red}(x_p) \text{ subject to } \Delta E^\ddagger(x_p) = \Delta E^\ddagger$$

No typical constrained optimization, three nested layers
From properties to structures, instead of from structures to properties

$$\min_{x_p} E_{red}^A(x_p) \text{ subject to } \Delta E^\ddagger(x_p) = \Delta E^\ddagger$$

Generates low energy catalyst structures with varying degrees of reactivity

Use Sequential Quadratic Programming

Each point on curve thought of as a different catalyst site

Different anchor point, A
Algorithm Formulation

Local quadratic expansion

\[
E(x^A_i + \Delta x^A_i, x_p + \Delta x_p) - E(x^A_i, x_p) =
\begin{bmatrix}
\Delta x^A_i \\
\Delta x_p
\end{bmatrix}
\begin{bmatrix}
g^A_i \\
g^A_p
\end{bmatrix}
+ \frac{1}{2}
\begin{bmatrix}
\Delta x^A_i \\
\Delta x_p
\end{bmatrix}
\begin{bmatrix}
H^A_{ii} & H^A_{ip} \\
H^A_{pi} & H^A_{pp}
\end{bmatrix}
\begin{bmatrix}
\Delta x^A_i \\
\Delta x_p
\end{bmatrix}
\]

Similarly for transition state

Minimize \(E(x^A_i, x_p)\) given any \(\Delta x_p\) by interior optimization

\[
\Delta x^A_i = -(H^A_{ii})^{-1}(g^A_i + H^A_{ip}\Delta x_p)
\]

Optimize interior atoms for given \(\Delta x_p\)

Move periphery atoms

Similarly for transition state
Reduced potential energy surface

\[ E_{\text{red}}^A(x_p + \Delta x_p) = E_{\text{red}}^A(x_p) + (\Delta x_p)^T g_{\text{red}}^A + \frac{1}{2} (\Delta x_p)^T H_{\text{red}}^A \Delta x_p \]

Find the lowest energy sites with a given activation energy

\[ \min_{x_p} E_{\text{red}}^A(x_p) \quad \text{subject to} \quad \Delta E^\ddagger(x_p) = \Delta E^\ddagger \]

Sequential Quadratic Programming

‘Dial’ the activation energy

\[ \Delta x_p \quad \Delta \Delta E^\ddagger \]

New catalyst site structure  Step in activation energy

Reactant state  † state

\[ \min_{x_i^A} \quad \opt_{x_i^A} \]

\[ E_{\text{red}}^A(x_p) \quad E_{\text{red}}^+(x_p) \]
How do typical active and dead sites differ?

Representative sites not up here

\[
\Delta x_p = - (H_{red}^A)^{-1} (g_{red}^A - \lambda \Delta g_{red}).
\]

\[
\lambda = \frac{\Delta \Delta E^\dagger + (\Delta g_{red})^T (H_{red}^A)^{-1} g_{red}^A}{(\Delta g_{red})^T (H_{red}^A)^{-1} \Delta g_{red}}.
\]
Off-pathway intermediate formation during ethene metathesis by isolated Mo(VI) on amorphous SiO₂

Handzlik used *ten* QM/MM models from β-cristobalite.

Handzlik’s *ten* ONIOM models from $\beta$-cristobalite

Our quadratic programming approach to model distribution of molybdenum sites on silica

periphery: terminal F atoms

basis deficient to mimic OH

interior: everything else

A broad distribution of active site structures are generated


Identify structural descriptors of activity
New framework for modeling amorphous catalyst sites

From properties to structures

Generate sites with different reactivity
Examine structure sensitivity

Contrast dead & active sites for descriptors

\[
\frac{<k>}{k_{\text{min}}} \approx 20 \text{ at } 310 \text{ K}
\]


Applying modeling to understand the synthesis, activity, and stability of catalysts

Modeling quenched disorder of catalyst sites on amorphous supports

Predicting the stability of supported nanoparticles
Increasing catalyst durability and recyclability is important

Pollution control

Chemical production & alternative energy

Many modes of deactivation

Selective poisoning

Non-selective poisoning

Fouling

Leaching

Ostwald ripening

Disintegration

Reactant

Monomers

Metal Particle

Support
Nanoparticle disintegration is a common phenomena

Rh/Al₂O₃


M. A. Newton,, Nat Mater 2007, 6, 528

M. Argyle Catalysts 2015, 5(1), 145-269
Nanoparticle disintegration can cause catalyst deactivation

\[ \text{C}_2\text{H}_4 + \text{CO} + \text{H}_2 \]

Rh/SiO\(_2\)

Most active size

Or, Nanoparticle disintegration can *redisperse agglomerated particles*

Rh/SiO$_2$
Energetics of supported nanoparticles

Metal nanoparticles have different exposed facets

What about the effect of reactants?

Average energy of particle per atom

\[ \Delta E_{\text{NP}} = \frac{3\Omega \gamma_{\text{me}}}{R} \]

Surface energy of metal particle

Surface energy of facet i

Area ratio of facet i

Image courtesy of Michael Engel
Reactant adsorption lowers particle surface energy

\[ \Delta E_{NP} = \frac{3\Omega\gamma_{me}}{R} \]

\[ \gamma_{me} = \sum_i f_i [\gamma_i + \Delta\gamma_i (T, P)] \]

\[ \Delta\gamma_i (T, P) = \frac{\theta_i [E^\text{ad}_x (\theta_i) - \Delta\mu_x (T, P)]}{A_i} \]

CO binding on (111) facet

Temperature ↓, Pressure ↑, Coverage ↑
Disintegration can be modeled by the Gibbs Free Energy

\[ \Delta G_{\text{disintegration}} < 0 \]

Ab initio thermodynamics

\[ \Delta G_{\text{disintegration}} (R, T, p) = G_{\text{adatom-complex}} - G_{\text{reactant}} - G_{\text{nanoparticle}} \]

Disintegration can be modeled by the Gibbs Free Energy

\[ \Delta G_{\text{disintegration}} < 0 \]

\[ \Delta G_{\text{disintegration}} (R, T, p) = E_f - \frac{3\Omega \Gamma_{\text{me}}}{R} - n \left[ \mu_x^0 (T, p_0) + k_B T \ln \frac{p_x}{p_0} \right] - TS \]

Ab initio thermodynamics

Formation energy of adatom complex

Standard gas phase chemical potential

Configurational entropy of complexes

Nanoparticle energy

Can we make qualitative predictions about nanoparticle disintegration that agrees with experiments?

- For supported Rh, Pd and Pt particles, which is most susceptible to disintegration?
- Among NO and CO, which one is more efficient for catalyst redispersion?
- Identify the dominant driving forces
- What are the stable species on the surface?

**Ab Initio approach to predict nanoparticle disintegration**
Science crossing borders

UC Santa Barbara

Dalian Institute of Chemical Physics

Evan Sanderson

Prof. Wei-Xue Li

Dr. Runhai Ouyang
Modeling procedure

- Projector Augmented Wave method
- RPBE Functional
- Plane wave kinetic energy cutoff = 400 eV
- Forces converged to 0.03 eV/Å
- Spin polarized

(4x2) Rutile TiO$_2$(110)

Vacuum layer thickness of 15 Å

Periodic model
Adatom formation energies are large and endothermic

\[
\text{Formation energy} = E_{\text{adatom/support}} - E_{\text{support}} - E_{\text{bulk}}
\]

Formation energy for Rh: 2.88 eV
Formation energy for Pd: 2.01 eV
Formation energy for Pt: 3.12 eV
Reactant binding stabilizes formation of adatoms

\[
\text{Formation energy} = 0.75 \text{ eV} \\
-1.35 \text{ eV}
\]
Rh(CO)$_2$ and Rh(NO)$_2$ have more favorable formation energies than Rh(CO) and Rh(NO)
Gas phase metal complexes not considered in disintegration analysis

- Higher order complexes also preferred gas phase
- These complexes not observed in experiments bound to support
- May play a role in gas phase ripening
Predicting particle disintegration under experimental conditions

For a 2 nm particle on TiO$_2$(110)

In agreement with experiment, Rh(CO)\(_2\) predicted to form but not Rh(CO)

For a 2 nm particle on TiO\(_2\)(110)


Rh/TiO$_2$(110) more responsive to CO and NO-induced disintegration than Pd or Pt

Experimentally\textsuperscript{[1]} Rh(CO)$_2$, $d < 60$ Å
Computed Rh(CO)$_2$, $d < 38$ Å

Isolated Metal Active Site Concentration and Stability Control Catalytic CO$_2$ Reduction Selectivity

Nanoparticle disintegration can be predicted using *ab initio* thermodynamics

- Rh/TiO$_2$(110) most susceptible to CO and NO-induced disintegration
- NO is a more efficient reactant for particle disintegration than CO
- Dominant driving force is adatom stabilization due to reactant binding


Towards understanding the activity and stability of catalysts

Systematic algorithm to model isolated amorphous sites

Predicting the stability of supported nanoparticles

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Questions?
Structural embedding

*Real site is embedded*, not isolated
- usually have electrostatic effects
- external matrix strain

Bias the distribution of $x_p$ pairs

$$g(r)$$

$$w(r) = -k_BT \ln g_{2nd}(r)$$

Si-O-Si: no need to modify
through-matrix forces

\[ \gamma_{me} \text{ is surface energy of metal particle} \]
\[ \gamma_{int} \text{ is interfacial energy between metal particle and support} \]
\[ \gamma_{ox} \text{ is surface energy of support} \]
\[ H_{adh} = \gamma_{int} - \gamma_{me} - \gamma_{ox} \text{ is adhesion energy between metal particle and support} \]
\[ \alpha \text{ is contact angle} \]

Exposed surface area of particle

\[ A_s = 2\pi R^2 [1 - \cos (\alpha)] \]
\[ \alpha = 90^\circ \rightarrow A_s = 2\pi R^2 \]
\[ \alpha = 180^\circ \rightarrow A_s = 4\pi R^2 \]

Contact interface area between particle and support

\[ A_{int} = \pi R^2 \sin^2 (\alpha) \]
\[ \alpha = 90^\circ \rightarrow A_{int} = \pi R^2 \]
\[ \alpha = 180^\circ \rightarrow A_{int} = 0 \]

Average energy \( \Delta E_{NP} \) (per atom) with respect to infinite size particle (bulk)

\[ \Delta E_{NP} = \frac{1}{N} \left[ (A_s + A_{int}) \gamma_{me} + A_{int} H_{adh} \right] \]

\[ N = \frac{4\pi R^3}{3} \left( \frac{\alpha_1}{\Omega} \right) = \text{Number of metal atoms in particle of interest} \]
\[ \alpha_1 = \frac{[2 - 3 \cos (\alpha) + \cos^3 (\alpha)]}{4} \]
\[ \Omega = \frac{4\pi r^3}{3\eta} = \text{Molar volume of bulk atom} \]
Configurational Entropy

\[ \Delta S = \frac{k_B}{N} \ln \frac{N_t!}{N!(N_t - N)!} \]

\[ = -k_B \left[ \ln \theta_{mc} + \left( \frac{1}{\theta_{mc}} - 1 \right) \ln \left( 1 - \theta_{mc} \right) + \frac{1}{N} \right] \]

\[ \approx -k_B \left[ \ln \theta_{mc} + \left( \frac{1}{\theta_{mc}} - 1 \right) \ln \left( 1 - \theta_{mc} \right) \right] \]
However, $\gamma(R)$ should likely be used in kinetic studies. Campbell, C. T.; P et al. Science 2002, 298, 811
Example: Coverage dependence of CO/NO binding on Rh (111) facet

$E_{\text{NO}}^{\text{ad}} = 0.4324\theta^2 + 0.2752\theta - 1.8989$

$E_{\text{NO}}^{\text{diff}} = 1.2972\theta^2 + 0.5504\theta - 1.8989$

$E_{\text{CO}}^{\text{ad}} = 1.5419\theta^2 - 0.6393\theta - 1.4615$

$E_{\text{CO}}^{\text{diff}} = 4.6257\theta^2 - 1.2786\theta - 1.4615$

$E_{x}^{\text{diff}}(\theta_i) = \frac{d[\theta_i \times E_x^{\text{ad}}(\theta_i)]}{d\theta_i} = \Delta \mu_x(T, P)$

Less pronounced difference between CO and NO binding for Pt and Pd

**NO adsorption positions**

**CO adsorption positions**
R. Chen et al., Comput. Theor. Chem. 2011

$\Delta \gamma_i(T, P) = \frac{\theta_i [E_x^{\text{ad}}(\theta_i) - \Delta \mu_x(T, P)]}{A_i}$
Surface coverage dependence of CO/NO binding on Pd, and Rh (111)

**NO adsorption positions**

**CO adsorption positions**

CO/NO bind strongest to Rh. $[\]d^8$ vs. $[\]d^9$
Modeling reduction in surface energy due to reactant adsorption

\[
\bar{\gamma}_{me}(T, P) = \sum_i f_i [\gamma_i + \Delta\gamma_i(T, P)] \approx \gamma_{me}^{111} + \Delta\gamma_{me}^{111}(T, P)
\]

Based on differential binding energy calculations.
Effects of chemical potential and particle size on particle energy

\[ \Delta \overline{E}_{NP} = \frac{3\Omega \overline{\gamma}_{(111)}}{R} \] contours

In the presence of CO

In the presence of NO

\[ \Delta \mu_{\text{CO}} \]

\[ \Delta \mu_{\text{NO}} \]
CO/NO adsorption sites on Pd/TiO$_2$(110)

$E^f_{\text{CO}}$ (mono) = 0.26 eV

$E^f_{\text{NO}}$ (mono) = -0.05 eV

$E^f_{\text{CO}}$ (di) = -0.54 eV

$E^f_{\text{NO}}$ (di) = -0.67 eV
CO/NO adsorption sites on Pt/TiO$_2$(110)

$E_{\text{CO (mono)}}^f = 0.09 \text{ eV}$

$E_{\text{NO (mono)}}^f = -0.10 \text{ eV}$

$E_{\text{CO (di)}}^f = -0.69 \text{ eV}$

$E_{\text{NO (di)}}^f = -0.67 \text{ eV}$
Also in agreement with experiment, $\text{Rh(NO)}_2$ predicted to form but not $\text{Rh(NO)}$

In the presence of NO

Gibbs free energy of disintegration (eV)

Pd and Pt not predicted to form adatom complexes (Under typical conditions)

$\text{Rh(NO)}_2$