Exploring the anomalous behavior of metal nanocatalysts with finite temperature AIMD and x-ray spectra

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Importance of Theoretical Simulations

Why Theory?
Access to structural and electronic properties
Separation of local and global domains

In particular, why Ab Initio Molecular Dynamics (AIMD)?
Importance of non-equilibrium states
Access to time-domain

Outline:
Importance of disorder in catalysis
Dynamics and electronic structure in XANES
Dynamics and structural disorder in EXAFS
Importance of Disorder in Catalysis
XAFS: Access to Average Local Properties

XANES: Access to average electronic structure

EXAFS: Access to average bond distances and disorder
Experimental (XAS, STEM, TPR, and XPS) and Theoretical (DFT) Characterization of Supported Rhenium Catalysts

S. Bare, S. Kelly, F. D. Vila, D. Boldingh, E. Karapetrova, J. Kas, G. Mickelson, F. Modica, N. Yang, J. J. Rehr


DFT/EXAFS model with three species was used to identify the dominant Re adsorption site on the alumina surface.

Re on γ-Al₂O₃
Dynamic structure in supported Pt nanoclusters: Real-time density functional theory and x-ray spectroscopy simulations

F. D. Vila, J. J. Rehr, J. Kas, R. G. Nuzzo, A. I. Frenkel

Physical Review B 78, 121404(R), 2008

Complex dynamics:
multiple-time scales, librational motion, fluctuating bonding

Simulations explain:
large structural disorder, Negative Thermal Expansion (NTE).

Pt$_{10}$ on $\gamma$-Al$_2$O$_3$
New Concept: Dynamic Structural Disorder (DSD)

**DSD drives:**

- Fluctuating bonding
- Cluster mobility
- Charge separation
- Layering and segregation
- Adsorbate dynamics (right)
- Adsorbate reactivity

**Inhomogeneity**


CO dynamics on Pt$_{10}$Sn$_{10}$
Disorder Affects Reactivity

$O_2$ dissociation on $\text{Pt}_{10}\text{Sn}_{10}$

Large differences in activation energy ($E_{\text{act}}$)
Reaction path depends on DSD
Dynamics and Electronic Structure in XANES
Theory: Static Simulations are Inadequate

$\text{Pt}_{10}$ on $\gamma$-$\text{Al}_2\text{O}_3$ @ 165 K

$+\delta$ ("Oxidized")

$-\delta$ ("Metallic")

MD simulations reproduce experiment

Vila et al. Physical Review B 78, 121404(R), 2008
Inhomogeneity in Well-defined (?) Nanoparticles

Bond contraction with heating/desorption
White line: redshift, Emission line: blueshift
EXAFS measurements: Predict truncated cuboctahedron Pt$_{37}$

Hypothesis: Both phenomena related to desorption
Is inhomogeneity important to these phenomena too?
Charge Inhomogeneity

**Pt₃₇ on Graphite**

- **Pt₃₇**
- **Pt₃₇ + CO (Edge)**
- **Pt₃₇ + CO (Face)**
- **Pt₃₇ + 15 CO (Top)**

**CO-Bound**

**Pt₃₇ on SiO₂**

- **Pt₃₇**
- **Pt₃₇ + CO (Edge)**
- **Pt₃₇ + CO (Face)**
- **Pt₃₇ + 15 CO (Top)**

**O-Contact**

CO-bound Pt atoms loose 0.2-0.3e each
Layer charge alternation
Bond Length vs Charge Inhomogeneity

\[ \Delta Q \]

\begin{align*}
\text{R}_{\text{PtPt}} & \quad 2.90 & 2.85 & 2.80 & 2.75 & 2.70 & 2.65 & 2.60 & 2.55 \\
\Delta Q & \quad +0.4 & +0.3 & +0.2 & +0.1 & +0.0 & -0.1 & -0.2
\end{align*}
Opposite trends: Qualitatively reproduce experiment
Dynamics and Structural Disorder in EXAFS
Negative Thermal Expansion (NTE) in smaller NPs
Large 0K ("static") disorder in smaller NPs
Apparent bond strengthening with NP size decrease

Sanchez et al. JACS 131, 7040, 2009
Anomalous Effective Grüneisen Parameter?

\[ \gamma = -\frac{1}{3} \frac{d \ln \nu_E}{d \ln R_{PtPt}} \]

\[ \Rightarrow \gamma \approx -\frac{1}{3} \frac{\Delta \nu_E}{\Delta R_{PtPt}} \frac{R_{PtPt}}{\nu_E} \]

Pt metal:
- Expt: \( \gamma = 2.7 \)
- Theo: \( \gamma = 2.8 \)

0.9-1.1 nm NPs:
- From Einstein Model Fit:
  - Expt: \( \gamma \approx 5\pm2 \)

Einstein Model with Static Disorder

\[ \sigma^2(T) = \sigma_s^2 + \frac{h}{8\pi^2\mu v_e} \frac{1}{\coth \left( \frac{h\nu_E}{2k_BT} \right)} \]

Effective Grüneisen parameter larger in NPs than bulk
Anomalous Effective Grüneisen Parameter?

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\[ \rho_R(\omega) \approx \sum_{i=1}^{N} w_i \delta(\nu - \nu_i) \]

\[ \bar{\nu}_E = \langle \nu^{-2} \rangle^{-\frac{1}{2}} = \left( \sum_{i=1}^{N} \frac{w_i}{\nu_i^2} \right)^{-\frac{1}{2}} \]
Anomalous Effective Grüneisen Parameter?

\[ \gamma = -\frac{1}{3} \frac{d \ln \nu_E}{d \ln R_{PtPt}} \]

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0.9-1.1 nm NPs:
- From Einstein Model Fit:
  - Expt: \( \gamma \approx 5 \pm 2 \)

Pt\textsubscript{37} on C:
- From Vib. Component:
  - \( \gamma \approx 1.7 \)

What is the origin of this discrepancy?
Anomalous Bond Strength from Einstein Model Fits

\[ \sigma^2(T) = \sigma_S^2 + \frac{h}{8\pi^2 \mu \nu_e} \coth \left( \frac{h \nu_E}{2k_B T} \right) \]

Einstein Model with Static Disorder

- 0.9 nm NPs: \( \nu_E \approx 6.3 \) THz
- 1.1 nm NPs: \( \nu_E \approx 4.6 \) THz
- Pt Foil: \( \nu_E \approx 3.8 \) THz

Sanchez et al. JACS 131, 7040, 2009
Computational Details

**Systems:**
- \( \text{Pt}_\text{10} \) and \( \text{Pt}_\text{20} \) clusters

**Support:**
- \( \gamma-\text{Al}_2\text{O}_3 \)
- 4 layers
- Dehydroxylated

**Cell:**
- \( 19.4 \, \text{Å} \times 13.7 \, \text{Å} \)
- 16 Å vacuum

**MD Setup:**
- 6 initial conditions
- 20 ps runs:
  - 10 ps thermalization
  - 10 ps analysis
- 3 fs time-step
- Nosé-Hoover thermostat

**Method:**
- PBE XC functional
- US PPs, 297 eV cutoff
- VASP
Total Mean Square Relative Displacement (MSRD)

\[ \sigma^2(T) = \langle (r - \bar{r})^2 \rangle = \frac{1}{\tau} \int_0^\tau [r(t) - \bar{r}]^2 dt \]

Reasonable agreement between theory and expt.
High (> 1THz) and Low (< 1 THz) Frequency Filtering

Filter Function:

\[ r_L(t) = \int_{-\infty}^{+\infty} r(\tau) F(t - \tau) \, d\tau \]

\[ r_H(t) = r(t) - r_L(t) \]

Filter Function:

\[ F(t) = \begin{cases} \frac{\pi}{2} v_L \cos(\pi v_L t), & |t| < \frac{1}{2} v_L \\ 0, & |t| \geq \frac{1}{2} v_L \end{cases} \]
Power Spectra of CM and Pt-Pt Dynamics

\[ \frac{d\sigma^2}{dv} = \frac{2}{\pi} \int_{0}^{\infty} \langle r(t) \cdot r(0) \rangle \cos(2\pi vt) e^{-\epsilon t^2} dt \]

\[ \langle r(t) \cdot r(0) \rangle = \frac{1}{\tau} \int_{0}^{\tau} r(t' + t)r(t') dt' \]

Nice separation of slow and fast dynamic regimes
Vibrational MSRD

\[ \sigma_H^2(T) = \frac{1}{\tau} \int_0^\tau [r_H(t) - \bar{r}_H]^2 dt \]

\( \nu_E \approx 4.1 \text{ THz} \)

Expt (0.9 nm)

Theo: Total

Theo: Vib

Pt Foil:
\( \nu_E \approx 3.8 \text{ THz} \)

0.9 nm NPs:
\( \nu_E \approx 6.3 \text{ THz} \)

Normal linear vibrational behavior
Dynamic Structural Disorder (DSD) MSRD

\[ \sigma_L^2(T) = \frac{1}{\tau} \int_0^\tau [r_L(t) - \bar{r}_L]^2 \, dt \]

Normal linear behavior: Low frequency quasi-harmonic modes
DSD: Correlation Between CM and Pt-Pt Dynamics

Moderate/strong correlation between CM libration and Pt-Pt bonds
Quasi-static MSRD: Anomalous Structural Disorder

\[ \sigma_{QS}^2(T) = \langle (r_L - \bar{r}_L)^2 \rangle \]

**Anomalous disorder (ASD): Causes apparent strengthening**

*Graph showing the relationship between temperature and disorder, with theoretical and experimental data points.*

**Legend:**
- **Expt (0.9 nm)**
- **Theo: Total**
- **Theo: Vib**
- **Theo: DSD**
- **Theo: QS**
Dynamic activation and depletion of long bonds
Effect of Support

Support accounts for \( \sim 50\% \) of disorder.
Disorder in Pt$_{20}$

Support less important in Pt$_{20}$
Grüneisen Parameter: NPs vs Bulk

\[ \gamma = -\frac{1}{3} \frac{d \ln \nu_E}{d \ln R_{PtPt}} \]

Pt metal:
- Expt: \( \gamma = 2.7 \)
- Theo: \( \gamma = 2.8 \)

Nanoparticle:
- From Einstein Model Fit:
  - Expt: \( \gamma \approx 5 \pm 2 \)
  - Theo: \( \gamma \approx 4 \pm 2 \)
- From Vib. Component:
  - \( \gamma \approx 1.4 \pm 0.2 \)

\[ \gamma \approx -\frac{1}{3} \frac{\Delta \nu_E}{\Delta R_{PtPt}} \frac{R_{PtPt}}{\nu_E} \]

Grüneisen Parameter: Enhanced by anomalous disorder
Summary

AIMD reveals:

Importance of Structural Disorder:
- In catalysis
- In EXAFS and XANES analysis

Single mechanism, dynamic activation, that explains:
- NTE
- Large disorder
- Bond strengthening

Normal behavior of Pt-Pt vibrations, but slightly stronger bonds
Coupling to CM motion → Dynamic disorder

Implications for interpretation of EXAFS:
Analysis must account for both ASD and DSD
Need new ASD modelling approach
Anomaly signature: $\gamma_{NP} > \gamma_{Bulk}$
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