

Utilizing Site-Dependent NO Reduction to Probe Step Sites on Supported Pt Nanoparticles

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Supported nanoparticles are characterized by size and site heterogeneity

Support

Chemisorption

Microscopy

Average particle size

Relies on limited images to conclude average size and distributions

Need a technique that can probe specific metal coordination environments

NO dissociation over Pt depends on site coordination

Activation Barrier (kJ mol⁻¹)

Site	Barrier (kJ mol ⁻¹)
Pt(111)	202
Pt(100)	107
Pt(110)	134
Pt(211)	100
Pt(410)	80
Pt(633)	168
Pt(637)	135

NO + * → N* + O*

- Terrace sites
- Step sites
- Corner sites

Can we use structure sensitivity of this reaction to probe sites with specific coordination over metal nanoparticles?

NO dissociation over pre-reduced Pt catalysts is self poisoning

DFT: NO dissociation is feasible on model step sites

NO dissociation probes step sites on supported Pt nanoparticles

Surface fraction of sites responsible for NO dissociation follow same trend as step sites as a function of particle size.

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Machine Learning Force Fields Applied to Modeling Silver Catalyst Reconstruction in Ethylene Epoxidation

Maria V. Zuniga. Collaborators: Eric Sarbacker, David W. Flaherty (Georgia Tech)

1. Machine-learned Force Fields Can Construct Models at Near-DFT Accuracy

FLARE Active Learning Approach

Take MD Step

- Update \tilde{r}_i
- Compute ϵ_i

Uncertainty < 5%?

Update Force Field

- Call DFT $H\psi = E\psi$
- Re-train

2. 'On-the-fly' Training of an Ag-O-Cl Reactive Force Field

a. Explore Surface Reconstruction

At reaction conditions (493 - 573 K, 2-80 kPa C₂H₄, and 10-100 kPa O₂), the surfaces of Ag catalyze form a partially oxidized layer.

Shell (Ag₂O_{cl})

Reconstructed < 2nm

Local environment

Core (Ag)

d = 80 - 100 nm

Goal: To explore how promoters, such as chlorine, influence:

- Surface restructuring
- Reactivity and population of selective O species

b. Capturing Local Environments with Nanoclusters

- Start with empty model
- Use previous model to train subsequent structures

Final Model

DFT calls decrease as the model integrates past environments into training

MD Setup: T: 523 K, NVT

Potential Energy DFT Calls

Simulation time (ns)

Coordination analysis (RDF) suggests atomic rearrangement

Pair Separation distance (Å)

Solvent-Induced Local Electric Field Effects in Lewis Acid-Containing Zeolites

Kelsey Levine. Collaborators: Bhavish Dinkar, Yuriy Román (MIT)

1. What is a zeolite?

Zeolites are microporous solid acid materials used for catalysis, separations, etc. Made of tetrahedral TO₄ building blocks, where T is a cation (typically Si or Al)

TO₄ Building block Pentasil unit Framework

Zeolite pore sizes and frameworks vary

FAU: Large pore (~7.4 Å)

MFI: Medium pore (~4.7 Å)

CHA: Small pore (~3.7 Å)

2. Solvents Affect Electric Fields in Zeolite-Catalyzed Reactions

Different solvents form various structures in different zeolite frameworks. It is hypothesized that the solvent impacts reaction rates by exerting an electric field, which alters the transition state energy.

Strength of field effect depends on solvent structure (ability to hydrogen bond)

Large Pore (>5nm)

Increased hydrogen bonding, increased field effect

3. The Stark Effect: Vibrational Frequencies Change with Electric Fields

$\tilde{\nu}_{C=O} = 0.702 |F_{solvent}| + 1689$

C=O Frequency / cm⁻¹

Solvent Field / (MV/cm)

- water
- chloroform
- dichloromethane
- methyl sulfoxide
- acetonitrile
- pentanitrile
- tetrahydrofuran
- dibutyl ether
- hexanes

We can measure the electric field by measuring the vibrational frequency of a probe molecule

4. Solvent Impact on Zeolite-Catalyzed Reactions

Controlled Variables

- Solvent Type
- Solvent / Zeolite Structure
- Zeolite Hydrophobicity

Electric Field (measure with DFT)

correlates with

Vibrational Frequency (measure with experiments & DFT)

- Transition state energy (ΔG^\ddagger) is influenced linearly by electric field ($E_{solvent}$) and difference in polarizability between IS / TS ($\Delta\beta$)
- $\Delta G_{solvent}^\ddagger = \Delta G_{no\ solvent}^\ddagger - E_{solvent} \cdot (\Delta\beta)$
- Simulating the field effect offers a feasible pathway for understanding solvent effects in zeolite-catalyzed reactions

Effects of Sulfur Exposure on Cu Speciation and NH₃ Storage in SSZ-13

Arigaa Zolboot. Collaborators: Rohil Daya(Cummins), William S. Epling (UVA)

1. Stronger NO_x emissions standards: a key to cleaner air

NO_x forms smog and reduces air quality.

NO_x emission standards for vehicles improved 98% since 1975.

US EPA, Smog Vehicle Emissions, 2025.

2. SCR reduces NO_x

H₂Cs, CO, NO_x, Soot, SO₂

DOC, DPF, Urea, SCR, AOC, H₂O, N₂

Selective Catalytic Reduction (SCR):

 $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$

Y. Shan et al., National Science Review, 8 (10), 2021.

How does sulfur exposure impact the SCR performance?

3. Sulfur impact on SCR rates

Hypothesis: Sulfur binds to Cu-dimers more strongly than Cu-monomers

$Z_2Cu_2O + nNH_3 \leftrightarrow Z_2Cu_2O(NH_3)_n$

$Z_2Cu_2SO_4 + nNH_3 \leftrightarrow Z_2Cu_2SO_4(NH_3)_n$

where n = 1,2,3,4,6,8

Identifying lowest energy structures using AIMD and DFT:

Initial guesses → Optimize with DFT → Optimized structures are input for AIMD → Pick 5 lowest energy structures at least 0.05ps apart → Optimize with DFT → Lowest energy structure

4. Sulfur-Cu Binding

2Al pairs that form Cu-dimers

Gibbs free energy distribution

1 σ

Mean

T = 673 K

T = 473 K

$Z_2CuOH + SO_2 \leftrightarrow Z_2Cu_2SO_4 + H_2O$

$Z_2CuOH + SO_2 \leftrightarrow Z_2Cu_2SO_4$

We used PBE functional for free energy calculation, the distribution changes mildly but the overall conclusion does not change.

At both low and high temperature, the dimer formation is favored.

5. Does sulfur affect the NH₃ storage for Cu-dimer species?

Phase Diagrams for non-sulfated and sulfated Cu-dimers

NH₃ desorbs at 850K for 200ppm NH₃

NH₃ desorbs at 700K for 200ppm NH₃

NH₃ desorbs at higher temperature in sulfated Cu-dimers than in non-sulfated Cu-dimers.

Solvent Induced Mobility in Ion Exchanged Zeolites

Mohan Shankar. Collaborators: David Flaherty (Georgia Tech), Siddarth Krishna (Wisconsin)

Solvents can adsorb to and mobilize ion-exchanged metals electrostatically tethered to aluminum substituted zeolites

Si, Al

Add Solvent

Bound State

Mobile State

We predict when these states are thermodynamically favorable by constructing free energy phase diagrams

Enumerate Symmetrically Unique Structures

1. Optimize structures with DFT

2. Dock structures in zeolite using VOID

3. Calculate free energies

Generate Zeolite-Containing Phase Diagrams

Optimize with DFT → Calculate free energies

Increasing Number of NH₃

Boltzmann weighting of solvated Palladium species at various water partial pressures relevant to Wacker Oxidation

(collaboration with Prof. Krishna's group at the University of Wisconsin)

Next Steps

Use machine-learned potentials for molecular dynamics to give us time-dependent information about these systems

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Allegro