

A systematic *ab initio* strategy for predicting structure-activity relationships in amorphous catalysts and supports



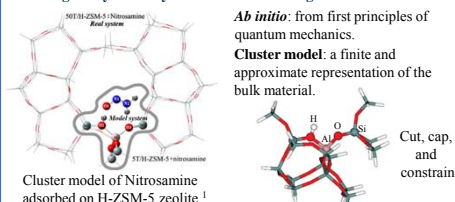
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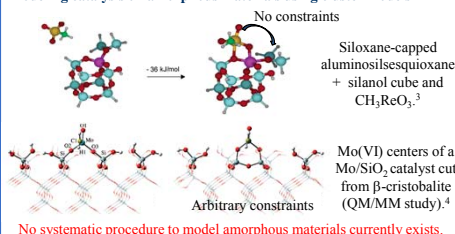
Background

Ab initio models for catalysis have been almost entirely aimed at understanding catalysis on crystalline materials. Catalysis on amorphous supports like silica-alumina are currently not amenable to systematic *ab initio* modeling. The problems stem from a diversity of local site environments and a lack of structural information of those environments.

Modeling catalysis on crystalline materials using cluster models

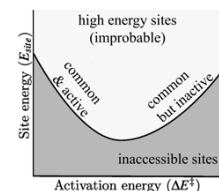
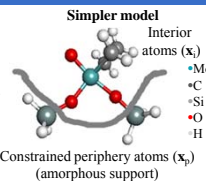


Modeling catalysis on amorphous materials using cluster models



Modeling premises

- 1) Solid so periphery atoms (\mathbf{x}_p) should be immobile
- 2) Periphery atom positions influence chemical properties of the site
- 3) Periphery atoms can be arranged in a continuous distribution
- 4) For any ΔE^\ddagger , assume low energy sites prevalent



Chemical properties depend only* on periphery atom placement

$$\Delta E^\ddagger(\mathbf{x}_p) = E(\mathbf{x}_i^\ddagger, \mathbf{x}_p) - E(\mathbf{x}_i^A, \mathbf{x}_p)$$

activation energy

transition state with optimized internal coordinates (\mathbf{x}_i^\ddagger) and fixed periphery (\mathbf{x}_p)

reactant state with optimized internal coordinates (\mathbf{x}_i^A) and fixed periphery (\mathbf{x}_p)

*and stick model topology. Similarly for Lewis acidity, hydration energy, etc.

KKT/SQP algorithm

Q: What is the lowest energy structure with a given chemical property?
A: Ugh... a **nested constrained optimization problem**. Need KKT/SQP.

KKT/SQP = Karush-Kuhn-Tucker/Sequential Quadratic Programming

Local quadratic expansion

$$E(\mathbf{x}_i^A + \Delta \mathbf{x}_i^A, \mathbf{x}_p + \Delta \mathbf{x}_p) - E(\mathbf{x}_i^A, \mathbf{x}_p) =$$

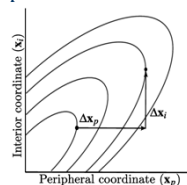
$$[(\Delta \mathbf{x}_i^A)^T (\Delta \mathbf{x}_p)^T] \begin{bmatrix} \mathbf{g}_i^A \\ \mathbf{g}_p^A \end{bmatrix} + \frac{1}{2} [(\Delta \mathbf{x}_i^A)^T (\Delta \mathbf{x}_p)^T] \begin{bmatrix} H_{ii}^A & H_{ip}^A \\ H_{pi}^A & H_{pp}^A \end{bmatrix} \begin{bmatrix} \Delta \mathbf{x}_i^A \\ \Delta \mathbf{x}_p \end{bmatrix}$$

and similarly for \ddagger

Minimize E^A given any $\Delta \mathbf{x}_p$ by internal optimization

$$\Delta \mathbf{x}_i^A = -(H_{ii}^A)^{-1} (\mathbf{g}_i^A + H_{ip}^A \Delta \mathbf{x}_p)$$

and similarly for \ddagger to remain at the saddle when \mathbf{x}_p changes



Reduced potential energy surface^{5,6}

$$E_{\text{red}}^A(\mathbf{x}_p + \Delta \mathbf{x}_p) = E_{\text{red}}^A(\mathbf{x}_p) + (\Delta \mathbf{x}_p)^T \mathbf{g}_{\text{red}}^A + \frac{1}{2} (\Delta \mathbf{x}_p)^T H_{\text{red}}^A \Delta \mathbf{x}_p$$

where

$$E_{\text{red}}^A(\mathbf{x}_p) = E(\mathbf{x}_i^A, \mathbf{x}_p) - \frac{1}{2} (\mathbf{g}_i^A)^T (H_{ii}^A)^{-1} \mathbf{g}_i^A$$

$$\mathbf{g}_{\text{red}}^A = \mathbf{g}_p^A - H_{pi}^A (H_{ii}^A)^{-1} \mathbf{g}_i^A$$

$$H_{\text{red}}^A = H_{pp}^A - H_{pi}^A (H_{ii}^A)^{-1} H_{ip}^A \quad \text{and similarly for } \ddagger$$

All internal atom degrees of freedom adiabatically follow stationary points that depend on the periphery coordinates. (the optimizations are now un-nested)

Find the lowest energy sites with a given activation energy

$$\min_{\mathbf{x}_p} E_{\text{red}}^A(\mathbf{x}_p) \quad \text{subject to} \quad \Delta E^\ddagger(\mathbf{x}_p) = \Delta E^\ddagger$$

Karush-Kuhn-Tucker gives sequential quadratic programming problem. (linearize the constraint function)

$$\begin{bmatrix} H_{\text{red}}^A & -\Delta \mathbf{g}_{\text{red}} \\ -(\Delta \mathbf{g}_{\text{red}})^T & 0 \end{bmatrix} \begin{bmatrix} \Delta \mathbf{x}_p \\ \lambda \end{bmatrix} = \begin{bmatrix} -\mathbf{g}_{\text{red}}^A \\ -\Delta \Delta E^\ddagger \end{bmatrix}$$

Solve directly for step size and activation energy constraint

$$\Delta \mathbf{x}_p = -(H_{\text{red}}^A)^{-1} (\mathbf{g}_{\text{red}}^A - \lambda \Delta \mathbf{g}_{\text{red}})$$

$$\lambda = \frac{\Delta \Delta E^\ddagger + (\Delta \mathbf{g}_{\text{red}})^T (H_{\text{red}}^A)^{-1} \mathbf{g}_{\text{red}}^A}{(\Delta \mathbf{g}_{\text{red}})^T (H_{\text{red}}^A)^{-1} \Delta \mathbf{g}_{\text{red}}}$$

Desired change in activation energy

$$\Delta \mathbf{g}_{\text{red}} = \mathbf{g}_{\text{red}}^\ddagger - \mathbf{g}_{\text{red}}^A$$

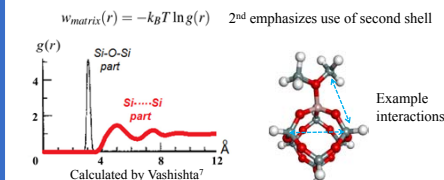
Quenched-disorder embedding

Include influence of surrounding matrix on \mathbf{x}_p atoms of the catalyst active site.

Ab initio modeling is computationally expensive.

Allows for use of smaller cluster models without neglecting extended structure interactions.

Influences KKT/SQP algorithm to generate a distribution of geometries consistent with structure factor of the surrounding matrix.



$$\hat{E}(\mathbf{x}_i, \mathbf{x}_p) = E(\mathbf{x}_i, \mathbf{x}_p) + \sum_{k=0}^{\text{pairs}} w_{\text{matrix}}(r_{ik}(\mathbf{x}_i, \mathbf{x}_p)) - \sum_{k=0}^{\text{pairs}} f_{\text{SiF}_4}(\mathbf{x}_i, \mathbf{x}_p)$$

Energy of embedded cluster

Energy of isolated cluster

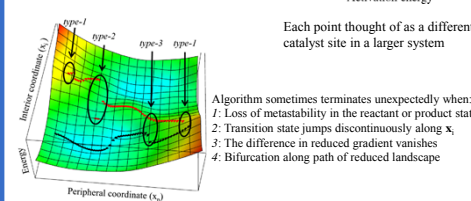
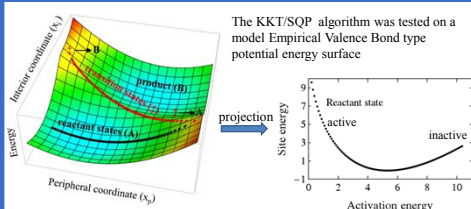
Influences from surrounding medium

periphery atom repulsion

Implemented a modified quasi-Newton optimization code to locate reactant and product stationary points with embedding.

Used an eigenvector-following code to locate the transition state.

Model potential energy surface

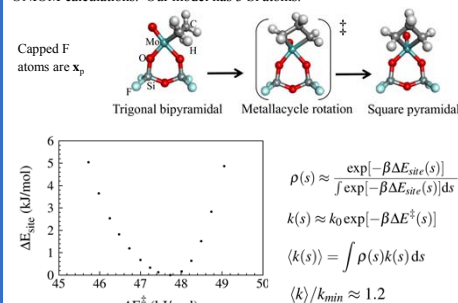


Acknowledgments

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Mo/SiO₂ ethene metathesis

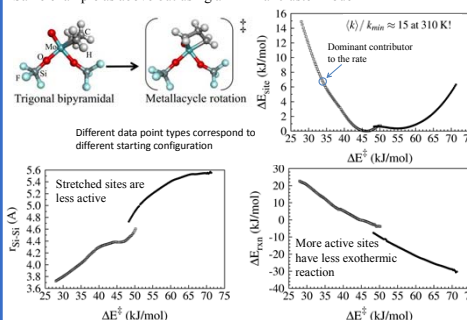
Handzik studied off-pathway intermediate formation in ethene metathesis by isolated Mo sites on amorphous SiO_2 .⁵ Handzik's models were carved from β -cristobalite with 35-49 Si atoms. He predicted $\Delta E^\ddagger = 46 \text{ kJ mol}^{-1}$ using ONIOM calculations. Our model has 3 Si atoms.



Strained structure restricts distribution of sites. Next example will show how accounting for inhomogeneity can change computed rate.

Generalized model

Same example as above but using a minimal cluster model



Conclusions

- Developed a systematic *ab initio* approach to model amorphous materials.
- Property-to-structure relationships (not structure-to-property).
- Introduced a quenched-disorder embedding procedure.
- Useful for understanding isolated sites in amorphous catalysts and supports.
- Accounting for inhomogeneity of sites can change computed rate.

References

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