Computational Modeling of Single-Atom Heterogeneous Catalysts for Clean Energy Solutions

Sanjubala Sahoo\textsuperscript{a}, Steven L. Suib\textsuperscript{a,c}, S. Pamir Alpay\textsuperscript{a,b}

\textsuperscript{a} Department of Materials Science & Engineering and Institute of Materials Science, University of Connecticut, 97 N Eagleville Rd. Storrs, CT 06269, USA
\textsuperscript{b} Department of Physics, University of Connecticut, 2152 Hillside Rd. Storrs, CT 06269, USA
\textsuperscript{c} Department of Chemistry, University of Connecticut, 55 N Eagleville Rd. Storrs, CT 06269, USA
Single Atom Heterogeneous Catalysts

Issues and Challenges:
- Designing novel heterogeneous catalysts with high activity and selectivity
- Replacing precious metal catalysts with earth abundant elements
- Catalytic poisoning leading to environmental pollution

Key Advantages of SACs
- **Optimum efficiency** could be gained in atomic level
- **Materials cost**: Using least volume of catalyst
- **Tunability**: Design properties of a catalyst based on need
- **New dimension**: Explore new science in materials due to reduced size leading unique electronic structure

Activity as a function of metal loading

Supports for SACs: Noble metals, Metal oxides, graphene

Relationship between catalytic activity and structural stability of SACs

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**References**
- Nat. Chem. 3, 634 (2011)
- Science 335, 1209 (2012)
- Science 344, 616 (2014)
Designing heterogeneous catalysts from theory

**Significance:** Predictions from computations drastically reduce number of possibilities that has to be attempted experimentally.

- **DFT** Accurately determines the GS properties of systems through the **charge density** by solving the **Kohn-Sham equation**

\[
\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ion}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{XC}}(\mathbf{r})\right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})
\]

- **Exchange-correlation potential**
  
  \[
  V_{\text{H}}(\mathbf{r}) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r' \quad \text{e-e repulsion term}
  \]

- **Exchange-correlation functional**
  
  \[
  V_{\text{XC}}(\mathbf{r}) = \frac{\partial E_{\text{XC}}[n(\mathbf{r})]}{\partial n(\mathbf{r})} \quad \text{Exchange-correlation potential}
  \]

- **Exchange-correlation functional**
  
  \[
  E_{\text{XC}}^{\text{LDA}}[n] = \int \varepsilon_{\text{XC}}(n) n(\mathbf{r}) d^3 r \quad \text{Exchange-correlation functional}
  \]

- **Electron charge density**
  
  \[
  n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 \quad \text{Electron charge density}
  \]

- **Wave function based methods:**
  - Hartree-Fock (overestimation of barrier)
  - Post Hartree-Fock (MP2, Coupled Cluster)
Designing heterogeneous catalysts from theory

DFT in Heterogeneous catalysis

Challenges from theory and computation

- Structural effects
  - Alloys
  - Compounds
- Electronic effects
  - Crystal structure
  - Surface faceting
  - Confinements
- Defects
  - Multisite functionalization
  - Nano structuring
- Strain
- Interface
- Tethering
- Co-adsorption
- Doping

HPC
Graphene as a support for SACs

**Our interest:** graphene based SACs for methane activation and conversion

- Zero gap semiconductor with high surface area, high electrical conductivity and strength
- Defects in Gr leads to several topological disorders\(^1\) which leads to change in their properties such as high adsorption energy\(^2\), high magnetic anisotropy\(^3\) etc.

Graphene electronic structure

- Linear dispersion in band structure leads to massless fermions where the electrons behave as relativistic particles obeying the Dirac equation. Such feature gives rise to *anomalous quantum Hall effect* and *ballistic transport*.

Electronic band structure of graphene showing Dirac cone feature (tight binding theory)

Graphene (TEM)

- Conduction band
- Dirac point
- Valence band

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\(^1\) Nat. Mat. **9**, 792 (2010)


SACs using graphene as a support

Applications of graphene

- Composites: 11%
- Bio-imaging & Bio-sensing: 5%
- Energy generation: 8%
- Energy Storage (Batteries & Supercapacitors): 19%
- Optoelectronic devices: 14%
- Synthesis & processing: 12%
- Electronic devices: 27%
- Others: 4%

Graphene based research publications

- RSC Adv. 4, 28987 (2014)

SACs with graphene support

- SACs with graphene support
- SACs using graphene as a support

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Methane activation and conversion

**Why methane:** It is the second most important greenhouse gas. Primary constituent of natural gas and a valuable clean-burning energy source.

**Sources of Methane emission**

**Challenge:** Direct conversion of methane requires high temperature due to the high bond strength. Finding a catalyst which could easily activate C-H bond in methane at relatively low temperature is a challenge.
Incorporation of TM atoms on graphene flake

- Carbon vacancy in Gr leads to Stone-Wale type defects leading to bending behavior
- Embedding TM stabilizes the hexagonal structure of Gr

Gr flake $C_{24}H_{12}$

Embedding TM

Co embedded in Gr

- Co shows maximum binding energy for both cases
- TM is slightly lifted for embedded case
- Methane is adsorbed with co-adsorbed TM-graphene

Gr sheet with C vacancy

Modeling graphene support

TM methane complex with graphene

- Presence of graphene enhances BE of CH₄
- Migration of TM (Cr, Mn, Cu) on graphene
- Charge transfer occurs from TM to surrounding atoms
- TM embedded case has maximum charge transfer compared to adsorbed case
Minimum energy reaction pathway has two spin states for (Cr, Mn, Fe)-methane where the low spin is preferable for the TS.

Spin crossover between high and low spin states

$E_A$ at low and high spin states are 0.24 eV and 1.31 eV, respectively.
Reaction path

Reaction pathway of methane activation for TM-graphene systems

• Graphene-supported systems are characterized by single-state reactivity
• Single Co atom on graphene is highly active for methane activation
Summary

• Graphene supported TM atoms show significant reduction in the activation barrier
• TM site acts as the catalytic active center
• The filling of three d-orbitals $d_{xz}, d_{yz}$, and $d_{z2}$ contribute to the catalytic activity
• Graphene supported Co catalyst most active for methane activation

Research in progress..

• Conversion of methane to methanol
• Investigating catalytic activity on other 2D supports
• Including temperature effect for catalytic reactions
Temperature effects for catalysis

Ab-initio thermodynamics applied to Ti in gaseous atmosphere

\[ \gamma (T, p) = \frac{1}{2A} [G(\text{slab}) - n_{\text{Ti}} \mu_{\text{Ti}} (T, p) - n_X \mu_X (T, p)] \]

\[ \mu (T, p) = \mu (T, p^0) + (1/2) k_B T \ln \left( \frac{p}{p^0} \right) \]

- \( \text{O}_2 \) and \( \text{H}_2 \) form passivating layers on Ti
- \( \text{O}_2 \) has stronger chemical affinity explaining the ubiquitous oxide layers in Ti
- Nitrogen diffuses into the bulk of Ti
- Clean Ti surface can be stabilized at \( \sim 1600 \text{ K} \) (at 1 atm).

Order of affinity of molecules on Ti surface: \( \text{O}_2 > \text{N}_2 > \text{H}_2 \)