Catalytic Reaction Rates from First Principles Simulations: Accelerating the Search for Better Catalytic Materials

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Heterogeneous Catalysis

Catalysis is vital to the chemical industry as well as sustainable energy conversion, storage, and use.

Catalyst: substance that increases the rate of a process without itself being consumed by the process.

Heterogeneous catalyst: reactants and catalyst in different phases.

Adsorption

Adsorption energies are not additive due to adsorbate-adsorbate interactions.

 clustered expansion fit to DFT

 where

 

\[ E(r_i) = J_i \sum_{j} \sigma_{ij} + \sum_{j,k} \sigma_{ijk} + \sum_{j,k,l} \sigma_{jkl} + \cdots \]

Cluster expansion calculates energies more than 1000x faster than DFT.

Large-scale Simulations

Monte Carlo simulations provide:
1. Statistical averaging of millions of surface configurations.
2. Effect of temperature and pressure.

Surface Heterogeneity

Site distributions are a manifestation of adsorbate-adsorbate interactions.

Rate Predictions

NO Oxidation

Rate-limiting dissociative adsorption of \( \text{O}_2 \) over catalytic Pt surface.

\[
\text{RDS: } 2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)
\]

Temperature Programmed Desorption

Associative desorption of \( \text{O}_2 \) from O-covered Pt surface.

Conclusions

Basis site model predictions agree with experimental results.

References