

# Structure and Dynamics of Heterogeneous Catalysts via Spectroscopy and Machine Learning

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Catalysis in the chemical industry underpins nearly all aspects of modern society, enabling the production of commodity chemicals, fuels, and high value products. Within the broader scope of catalysis, the lion's share of production goes to heterogeneous catalysts. In the analysis of these materials, computational catalysis has emerged as a cost-effective, robust method providing insights into the atomic-level structure and energies, enabling rational interpretation and design. However, much of this computational approach has been the product of static density functional theory (DFT) calculations, which miss many of the rich dynamic, anharmonic, and ensemble-based characteristics of real systems. This thesis aims to bridge these gaps by exploring the vast configurational spaces and the dynamic behavior of catalytic systems through finite-temperature atomistic simulations, spectroscopy, and machine learning.

In chapter 2, we investigate the structure of supported  $\text{MoO}_x / \text{Al}_2\text{O}_3$  catalysts under varying degrees of hydration and Mo loading using *ab initio* molecular dynamics (AIMD) and DFT. We spectroscopically model the system using AIMD as a benchmark for DFT and provide insight into how, under certain hydrated conditions, DFT excels as an inexpensive method for computing vibrational frequencies, while under dehydrated conditions, it is susceptible to the

largest errors. Computational and experimental IR and Raman spectra of the catalysts synthesized are compared under the same conditions.

In chapter 3, we circumvent the combinatorial challenge of finding low energy structures through the use of machine learning potentials (MLP). We develop a custom basin-hopping search algorithm to perturb the system of vanadium oxide clusters supported on titanium dioxide at intermediate coverages up to a monolayer. The most stable structures obtained from an MLP are then optimized with DFT to examine their electronic properties. We find that even at coverages up to 3/4 of a monolayer, it is possible to form highly active monomeric species when there is a vacancy in the TiO<sub>2</sub> support and an oxygen atom adsorbed on the surface.

In chapter 4, we introduce the Python Modulation Excitation Spectroscopy (PyMESpec) toolkit, an open-source library for analyzing MES experiments. PyMESpec offers fast and flexible baseline correction, phase-sensitive detection (PSD), chemometric deconvolution, and automated reaction rate extraction. PyMESpec applies to large datasets from spectroscopies and transient experiments in general. We demonstrate its capabilities on spectra from diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) over CeO<sub>2</sub> and modulation excitation ultraviolet-visible (ME UV-vis) and near-ambient pressure x-ray photoemission spectroscopy (NAP-XPS) on vanadia/titania catalyst for oxidative propane dehydrogenation.

In chapter 5, we reveal the complex dynamics of ceria-zirconia through molecular dynamics simulations with an MLP that delineates competing oxygen-diffusion mechanisms, with optimal mobility at intermediate reductions. We additionally expose a compensation between vacancy availability and lattice distortion at intermediate to high reductions and Frenkel defects at low reductions, underscoring a potential deficiency of <sup>16</sup>O/<sup>18</sup>O exchange experiments in deducing oxygen mobility.