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Entropic Effects on Microkinetic Modeling and for Catalyst Structure Prediction via DFT, Theory, and Machine Learning

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Highlights
- We identify correlations among vibrational frequencies of chemisorbates on transition metals
- We develop a theory of vibrational scaling and elucidate the physical origin of scaling slopes
- Scaling frequencies on surfaces significantly impacts equilibrium constants and microkinetics
- Machine learning is used in conjunction with DFT and the scalings for catalyst identification

1. Introduction

A breakthrough in computational catalysis was the introduction of linear scaling relations (LSRs), by Nørskov and co-workers,[1] which link the binding energy of a partially hydrogenated adsorbate AH_X to the binding energy of its respective atomic adsorbate or heteroatom across transition metal surfaces. LSRs provide a means to estimate thermodynamic properties of reaction intermediates on heterogeneous catalyst surfaces, enabling *in silico* catalyst screening.

A universal understanding of chemisorbate vibrations has not be demonstrated in literature and as such, metal-dependent vibrational effects are not currently applied to microkinetic modeling and materials prediction. In this work, we combine density functional theory (DFT), theory, and machine learning to accomplish this for the fist time.

2. Methods

We calculated binding energies and vibrational frequencies using the Vienna ab initio Simulation Package (VASP) version 5.4 with the projector augmented wave method (PAWs). We employ the RPBE density functional with D3 dispersion corrections. Simulation methods were similar to those of our previous study, including use of spin-polarized calculations for gas-phase species and ferromagnetic metals, a 3x3x1 Monkhorst-Pack k-point sampling grid for all slab calculations, and a 400 eV plane wave cutoff. The initial magnetic moments for each atom in spin-polarized calculations were set to VASP default values.

For gas calculations, the supercell size was 10x10x10 Å. A Brillouin zone was sampled at the gamma point; a 0.005 eV/Å force cut-off was used in geometry optimizations. For slab calculations, the force cut-off was set to 0.02 eV/Å with 20 Å of vacuum space. The periodic cell consisted of four layers with 16 metal atoms in each layer; the bottom two layers were fixed at their bulk values, determined using a 15x15x15 k-point grid using the tetrahedron method with Blöchl corrections. Bulk metal lattice constants were pre-optimized with DFT using the Birch–Murnaghan equation of state.

We study adsorption at the fcc hollow, bridge, and atop sites of (100), (110), and (111) transition metal facets and develop algorithmic criteria for assigning normal modes to specific vibrations. By combining effective medium theory (EMT), linear muffin-tin orbital (LMTO) theory, and the d-band model we decouple the contributions of the transition metal d-band and sp-band to surface induced adsorbate vibration for these facets. We apply the developed theory to generate descriptors that can be used in conjunction with machine learning algorithms to better understand in-situ experimental catalyst experiments. Algorithms

explored include support vector machines and decision trees for classification, as well as gaussian processes and neural networks for regression.

3. Results and discussion

We predict vibrational scaling relation (VSR) slopes and compare to first principles calculations. As shown in Figure 1, these predicted slopes span a wide range of values and have varying levels of influence on the thermochemical models used in identifying high-performing catalysts. By building a database of high resolution electron energy loss spectroscopy (HREELS) data covering 40 different combinations of chemisorbates and metal surfaces, we verify that such vibrational scaling relations exist experimentally as well.
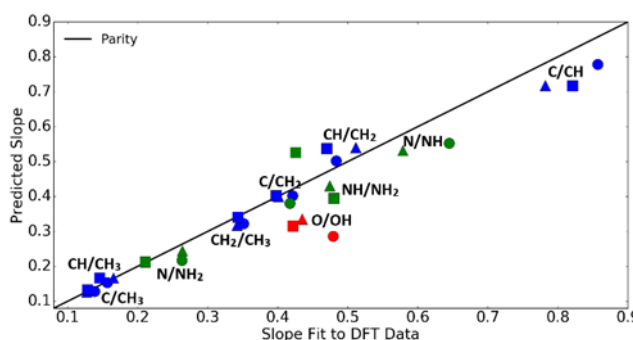

Figure 1. Predicted VSR slopes for AHX species represented as adsorbate A/B for CHX (blue), NHX (green), and OHX (red).

We extend our theory to larger molecules and demonstrate how scaling frequencies can be used in interpreting experimental infrared spectroscopy (IR) spectra. Analysis of IR data is particularly important for complex catalysts, such as bimetallic catalysts, where the exact surface structure is unknown, making first principles calculations infeasible without further understanding of the catalyst termination, the surface species present, their concentrations, and their preferred adsorption site. We demonstrate this spectral deconvolution using machine learning. Finally, we show that including the scaling relations developed here can impact coverages of adsorbates and microkinetic modeling. We demonstrate this for CO oxidation in a fuel cell.

4. Conclusions

By combining previously reported experimental data and our own DFT calculations, we reveal surface induced frequency shifts and develop theory to explain these shifts. Such shifts significantly affect equilibrium constants and surface coverages of competing chemisorbed species on varying transition metal surfaces. We validate these results with HREELS experiments and identify fingerprints for describing catalyst sites and catalyst structure.

References

[1]   F. Abild-Pedersen et al., Phys. Rev Lett. 99 (2007) 016105-1 – 016105-4