Advanced Predictive Modeling of Bimetallic Catalyst Behaviors through Cluster Expansion and Monte Carlo Simulations

Chen Jiachen[1], Dmitry Sharapa[1], Philipp N. Plessow[1*]

[1]Karlsruhe Institute of Technology (KIT), 76344, Karlsruhe, Germany

E-Mail presenting author: chen@kit.edu

Pt, Pd, and PtPd alloy nanoparticle catalysts are crucial for controlling automobile exhaust emissions. To understand the effects of external conditions, such as gas-phase composition and metal-support interactions, on these alloy particles, identifying active sites and mechanisms of deactivation like sintering is essential. This study examines the structure and properties of PtPd alloy nanoparticles on flat surfaces using density-functional theory (DFT) calculations at the BEEF-vdW level to explore adsorption properties and surface segregation. These calculations form the base for a cluster extension model, which, combined with Monte Carlo simulations, provides insights into surface segregation and catalytic activity changes under reaction conditions.

The cluster expansion model's accuracy is demonstrated with a mean absolute error of 0.0166 eV for CO adsorption energy at the fcc position, and it accurately predicts various properties, including vibrational frequencies of CO adsorption. Monte Carlo simulations of slab surface composition as a function of temperature reveal that CO presence at low temperatures increases Pt content on the surface, while temperatures above 400 K show no effect on surface composition. This comprehensive approach aids in understanding catalysts for emission control on larger temporal and structural scales.

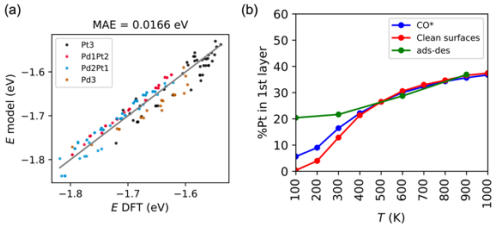

Figure 1: (a) Model predictions for adsorption energy, compared to DFT calculations. The figure shows CO adsorption at the fcc site, with different colors indicating the different compositions that make up the fcc site. (b) The variation of the composition of the alloy surface with temperature under different conditions simulated using the Monte Carlo method. The red line indicates a clean surface, the blue line indicates a fixed location on the surface where CO is adsorbed (coverage of 1/4), and the green line indicates that adsorption and desorption were considered (coverage from 0 to 1/4).