IDENTIFYING ACTIVE SITES OF THE WATER-GAS SHIFT REACTION OVER SUPPORTED PLATINUM CATALYSTS UNDER UNCERTAINTY

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Abstract

A novel combined top-down and bottom-up modeling approach has been developed for integrating computational and experimental kinetic data and to identify active sites and reaction mechanisms in catalysis. Three qualitatively different models regarding the active site for the water−gas shift reaction on titania supported Pt catalysts, Pt(111), an edge interface site, and a corner interface site, are tested against experimental kinetic data from multiple research groups. Uncertainties associated with density functional theory (DFT) calculations and model errors of microkinetic models of the active sites are informed and verified using Bayesian inference and predictive validation. Significant evidence is found for the role of the oxide support in the mechanism. Positive evidence is found in support of the edge interface active site over the corner interface site.

Keywords

Active site, water-gas shift, uncertainty quantification.

Introduction

Key bottlenecks in the rational design of novel heterogeneous catalysts are our limited ability (i) to integrate experimental, kinetic data with computational, first-principles models and (ii) to identify the relevant active sites on the catalyst. In this paper, a framework for overcoming these bottlenecks is presented and applied to the water−gas shift reaction (WGS: $CO + H_2O \rightleftharpoons CO_2 + H_2$) over Pt catalysts supported on titania. Considering that kinetic data such as the turnover frequency and its temperature and pressure dependence are some of the most important parameters characterizing a heterogeneous catalyst, it is these computational and experimental data that we aim to correlate for the identification of active sites.

Our overall strategy follows a combined top-down and bottom-up modeling approach (Walker et al. 2018). Here, top-down modeling corresponds to traditional chemical engineering modeling where a reaction mechanism is proposed, and all rate parameters are fitted to experimental data. While such an approach leads to a model that "fits" the experimental data and can often be used to interpolate between measured reaction conditions, such a model does not allow to determine a reaction mechanism or "characteristic" active site in the experiments considering that the large number of parameters permit one to colloquially "fit an elephant". In other words, the actual insight gained from the model is often very limited.

Bottom-up modeling is the conventional computational catalysis approach, where a reaction mechanism and microkinetic reactor model is proposed and all reaction rate constants are determined from first principles (usually DFT and harmonic transition state theory). While such a model permits predicting the relative activity of various mechanisms and thus, permits obtaining insight into the reaction mechanism for a given active site model,

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quantitative agreement with experimental data can usually not be achieved due to significant uncertainties in, e.g., the DFT energies, such that it is very challenging to compare characteristic active site models and even reaction mechanisms. In other words, the value of the bottom up modeling approach is limited by a significant uncertainty if a proper catalyst model has been selected.

In combined bottom-up and top-down modeling, the conventional computational catalysis approach is employed to determine a model for the kinetic parameters of a characteristic active site that depends on DFT energies such as the energy of a transition state or intermediate state. To obtain the correlation structure of the DFT energies, we perform DFT calculations with multiple, qualitatively different functionals and build a latent variable model for the energies of all transition and intermediate states. As a result, we obtain a microkinetic model that predicts kinetic parameters of an active site model with uncertainty.

Next, we use experimental kinetic data and calibrate (Bayesian calibration) our uncertain parameters against the experimental data. Applying this approach to multiple active site models, we can now compare the *evidence* of each active site model at new reaction conditions (data that have not been used during calibration) to determine if an active site model can capture the experimental data significant better than another one (by computing the Bayes factor). This approach also permits identifying reaction mechanisms and rate controlling steps under uncertainty.

Results

We applied the approach outlined above to the water-gas shift reaction over Pt-TiO$_2$ catalysts. A Pt(111) active site model cannot capture the experimental data from Kalamaras et al. (2009), Thinon et al. (2009), and Pazmino et al. (2012) and cannot be the active site under reaction conditions. Only for an edge interface active site model do we find positive evidences as per Jeffreys' scale (Jeffreys, 1939) and squared Mahalanobis distances, smaller than 12.59. In other words, only for the edge interface site do we find consistencies between model predictions and calibration and validation data at 0.05 significance level. The characteristic active site in the experiments from Kalamaras et al., Thinon et al., and Pazmino et al. are the same. Even in the presence of uncertainty can we identify the CO-promoted redox mechanism to be dominant for the WGS on edge, interface sites and only at temperatures above 573 K does the classical redox mechanism contribute significantly to the overall rate. Finally, water and surface O-H bond dissociation steps are the main rate controlling steps under reaction conditions.

Acknowledgments

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