Descriptors for solid catalysts: 21st century discovery tools

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Summary

This thesis focuses on the development of methodology for the use of descriptor-performance relationships for solid catalysts. In contrast to the situation in homogenous catalysis, where this type of methodology is mature and well established, descriptors for solid catalysts are still in a very early stage. With the present availability of parallel reactor systems, generating large and consistent data sets is no longer the bottleneck for this approach. In reality, processing modeling and utilizing the data to its maximum extent are the limiting steps.

We start from the very basics, generating a data set for the hydrogenation of 5-ethoxymethyl furfural (EMF) as an example. This data set was generated systematically, varying catalyst composition, temperature and solvent. The experiments were done using a parallel fixed bed reactor setup. This data set was was first explored in a traditional manner using conversion-selectivity plots. Subsequently, the data set was modeled using principal component analysis (PCA). The trends identified by the two methods are remarkably similar. PCA is a method that is fast and requires little specific expertise from its user. For that reason, a good practice for the evaluation of larger data sets is to first use PCA to identify major trends and outliers. After this, the conventional conversion-selectivity plots can be made, focused on trends that have been brought forward by the first analysis.

When it comes to descriptors for solid catalysts, the amount of previous research that can be built upon is limited. This holds true especially for the type of descriptors we focus on. Our main efforts are on identifying simple descriptors, that do not require long calculation times. This rules out the use of extensive computational chemistry methods. The second constraint we have imposed is that we want to be able to derive descriptors *a priori*, without first having to synthesize any catalyst. This constraint rules out the use of catalyst characterization to obtain descriptors. That said, both catalyst characterization and computational methods are very useful when developing descriptors. The general approach applied is to use a data set that has been derived via time-consuming methods to derive empirical models that in turn can be rapidly deployed to derive descriptors for a new set of catalysts, without a need to redo the time-consuming work.

To demonstrate this approach we developed empirical models that correlate heats of chemisorption (a key step in most solid-catalysed reactions) to descriptors for a diverse set of metals and adsorptives. The heats of adsorption we used were published data, calculated using density-functional theory (DFT). We combined this DFT data set with our descriptors, building an empirical model. This model works remarkably well, and can predict well also experimental adsorption parameters. Moreover, based on adsorption measurements for real catalysts, the methodology is easily extended to cover data from characterization.

The actual capabilities of descriptors-performance relationships are demonstrated using another example. Here we developed a set of descriptors based on Slater-type orbitals (STOs) and correlated these to the data obtained for the selective hydrogenation of 5-ethoxymethyl furfural. Both mono-metallic and bi-metallic catalysts are well captured by the models generated. More importantly, the results demonstrate that our descriptor methodology can be applied to a complex reaction network with multiple parallel and sequential reaction steps.

Ultimately, the application for this work is in making the process of discovering new solid catalysts. Our methods, although not yet fully developed, have already proven themselves in a number of applications. Although ideally suited for combination with parallel reactor equipment, the methods can also be applied to smaller data sets generated in conventional ways. While modeling will never eliminate the skilled interpretation of chemists and engineers, the modeling methods demonstrated do provide added value in the fact that they are unbiased and can give additional insights and ideas.