ABSTRACT

Dehydrogenation is a common reaction used to upgrade paraffins to olefins in the chemical and oil industries. Given the increased abundance of inexpensive alkanes due to the worldwide shale gas boom, this reaction has become increasingly important. Conventional industrial techniques such as thermal cracking and steam cracking have relatively poor olefin selectivity and thus require energy-intensive separations. Industry is increasingly relying on catalytic dehydrogenation as a more environmentally friendly alternative to generate olefins. While recent development in catalyst materials has largely solved issues with activity and selectivity, issues with catalyst stability remain. Deactivation mechanisms such as coke formation and phase changes plague the short-term and long-term stability of these catalysts, often requiring frequent and intensive regeneration procedures.

This thesis will explore several strategies for mitigating the deactivation of dehydrogenation catalysts. This includes the modification of catalyst properties and reaction conditions, such as the catalyst support and the use of H_2, to mitigate coke formation and even regenerate catalyst materials non-oxidatively, thus increasing the catalyst lifetime. Secondly, this thesis will cover the discovery of new catalyst materials through computational predictions based on descriptors assessed from several previous works. Experimental validation of these predictions led to the discovery of several new Rh and Ir based alloy materials that are remarkably selective and stable for propane dehydrogenation (PDH). Lastly, the contribution of electronic structure of PDH catalysts will be assessed using a new characterization technique that will help relate catalyst properties to catalyst performance and stability.

Several advanced X-ray synchrotron techniques have assisted the analysis and discovery of catalyst materials in this work. Particularly, this includes difference-EXAFS to assess the surface structure of alloy catalyst materials as well as the newly-developed non-resonant X-ray emission spectroscopy (NR-XES) to assess the electronic structure of the 5d valence band for Pt catalyst materials. To extend this work further, the goal is to apply this new technique to additional catalyst materials, such as Pt alloys or single site Pt supported on CeO_x, in order to measure the effect of different adsorbates on the electronic structure of the Pt catalyst. This will help derive fundamental insights to drive the development of the next generation of stable dehydrogenation catalyst materials.