Density Functional Theory Studies of Supported Single-Site Catalysts for Alkane Dehydrogenation

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Introduction

Dehydrogenation of light alkanes to olefins is an important chemical reaction primarily used to produce feedstocks for polymer industries. Currently Pt-Sn/Al2O3 and CrO3/Al2O3 are commercially used as alkane dehydrogenation catalysts. However, Pt is an expensive noble metal and chromium is environmentally hazardous, which make them unsuitable for sustainable applications. Alternative catalysts based on earth abundantly materials are, therefore, highly sought after. In this presentation, we will talk about our recent progress towards designing silica supported single site catalysts for selective alkane dehydrogenation. Particular emphasis will be given on the role of metal/support interaction in determining catalysts activity and selectivity. Detail mechanistic studies of catalytic alkane dehydrogenation as well as side reactions leading to undesired by-products will be discussed. Finally, a descriptor based approach of designing more efficient single-site dehydrogenation catalysts will be introduced.

Methods and Models

B3LYP hybrid density functionals with valence triple-zeta quality basis set (TZVP) was used for the calculations. Localized cluster models as well as periodic slab models were used to represent amorphous silica and zeolite supports. The accuracy of the models and methods were tested using an extensive set of test calculations.

Results and Discussion

Silica supported single site catalysts containing first-row transition and non-transition metals (Sc-Ga) have been studied to understand the structure of catalyst active site, metal coordination number and oxidation state, reaction mechanism, origin of catalysts activity and selectivity, based on which a descriptor based screening approach have been developed to design new catalysts with improved activity and selectivity.

Our studies show that the siloxane rings on silica play key role in determining the binding site for some of the metals. For example, Zn2+ and Co2+ preferentially bind with the strained defect rings present on silica surface. In addition, the siloxane rings also play major role in determining the structure of the catalyst active site. In general, the number of metal-oxygen bonds with the support increases when large siloxane rings are present and vice-versa. Therefore, the temperature at which the catalysts are thermally pretreated is important for determining overall activity as coordinatively unsaturated metal sites often result in higher activity.

There is no redox mechanism involved for the activation of H2 during hydrogenation and alkane during dehydrogenation. Instead heterolytic cleavage of H–H or R–H bond over the M–O bond is energetically preferred. There is also energetic preference for the activation of primary over secondary C–H bonds. Catalytic hydrogenation follows Eley–Rideal type mechanism in which H2 is activated first to form a metal hydride intermediate, while dehydrogenation mechanism is microscopic reverse of the hydrogenation mechanism. Calculations suggest that pathways which involve the formation of metal-hydride intermediates are energetically favorable, which has been verified using UV-Raman spectroscopy for some of the metals.

Figure 1. Mechanism of propane dehydrogenation over single-site Zn2+/SiO2 catalyst.

Reaction networks of possible side reactions involving deep dehydrogenation and C–C bond cleavage have been established which help to understand the origin of high selectivity in all of our single site catalysts. Finally, a descriptor based computational screening approach towards designing improved single site metal catalyst for alkane dehydrogenation has been developed.

Significance

Alkane dehydrogenation is a commercially important reaction and there is a growing demand for replacing current set of catalysts involving expensive noble metal or toxic element. Our theoretical studies towards understanding the structure-activity relationship of supported single site catalysts containing earth-abundant metals will help to optimize performance of an existing catalyst and design new catalysts with improve activity and selectivity.

References