

FIRST PRINCIPLES ANALYSIS OF CATALYTIC ALKANE DEHYDROGENATION REACTIONS

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The discovery of shale gas, along with advancements in extraction technologies, has transformed the hydrocarbon processing industry. Shale gas mainly consists of methane, ethane, propane, and trace amounts of longer chains of alkanes. Ethane and propane from shale gas can be converted into valuable chemicals like ethylene and propylene, which are important precursors for numerous industrially relevant chemicals. Conventionally, light olefins such as ethylene and propylene are produced via steam cracking or fluidized catalytic cracking of naphtha and natural gas. However, these processes face significant challenges, including suboptimal yields and energy-intensive operations. Heterogeneous catalytic dehydrogenation (DH) has emerged as a promising alternative, offering improved conversion and selectivity for the light olefin products. Optimizing these catalytic processes requires fundamental understandings of the structure-function relationships of the catalyst surface structures. Density functional theory (DFT) calculations are instrumental in exploring the thermodynamically stable surface structures and assessing their catalytic properties under relevant reaction conditions.

There exist two major categories of DH reaction, non-oxidative and oxidative. This study investigates the surface structures of platinum-based alloy catalysts, which are of particular interest for non-oxidative propane DH reaction due to their excellent catalytic performance. While Pt-Mn and Pt-Zn alloys, alongside established commercial Pt-Sn catalysts, offer improved selectivity, challenges such as catalyst deactivation due to coking and suboptimal yield remain unresolved. The precise surface structures of these alloys, including surface composition, and local atomic ordering effects such as segregation, islanding, and site isolation, are not yet fully understood. To address these knowledge gaps, DFT-derived interatomic potentials are developed using cluster expansion fittings, and Monte Carlo simulations are performed to systematically investigate the surface structures of these Pt-based alloy catalysts. This integrated approach enables efficient exploration of the large configurational space of Pt and Sn/Mn/Zn atom arrangements, capturing the influence of metastable surface structures on catalytic performance. Our findings provide

molecular-level insights into how alloy surface configurations impact propane conversion and propylene selectivity at elevated temperatures.

Recent investigations into oxidative chemistries have identified alternative oxidants such as S_2 , which notably minimize over-oxidation of target light olefins during DH reactions, as compared to conventional O_2 -driven processes. Experimental studies demonstrate that sulfurized Fe_3O_4 catalysts, particularly those with FeS_2 surfaces, achieve exceptional high ethylene yield in ethane DH reaction. In this context, DFT calculations are employed to investigate the surface structures of FeS_2 catalysts under S_2 -driven DH conditions, examining various surface terminations and sulfur-decorated configurations. These results highlight that surfaces decorated with sulfur dimers are thermodynamically favored under reaction conditions. Further mechanistic analysis reveals that S_2 -driven ethane DH occurs via a competitive mercaptan-mediated Mars-van Krevelen pathway. Additionally, the origin of enhanced propylene selectivity in S_2 -driven propane DH over alumina-supported vanadium catalysts is investigated. The study demonstrates that V–O sites promote deep DH to the desired product, propylene, in O_2 -driven reactions. Conversely, when isolated vanadium sites get sulfided, the thermodynamic driving force for overoxidation is diminished, thereby enhancing propylene selectivity in case of S_2 -driven propane DH reaction.

Collectively, these findings elucidate how distinct catalyst surface motifs govern the energetics of both selective and non-selective reaction pathways in ethane and propane DH reactions. This knowledge is instrumental for the rational design of stable DH catalysts and the optimization of reaction conditions aimed at maximizing the yield of desired light olefin products.