## Atomistic insights into highly dispersed catalysts for selective shale-gas chemistry

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Light olefins such as ethylene and propylene are essential building blocks in the chemical industry and are traditionally produced through energy-intensive processes like steam and fluid catalytic cracking of petroleum-based feedstocks. The emergence of shale gas extraction offers a lower-cost, alternative feedstock rich in ethane and methane. Ethane can be upgraded to ethylene via catalytic ethane dehydrogenation (EDH), while methane, which accounts for roughly 25% of global warming, poses an environmental challenge. Its effective utilization is critical to realizing the full potential of shale gas. Dry reforming of methane (DRM) offers a pathway to convert both CH<sub>4</sub> and CO<sub>2</sub> into syngas. While EDH and DRM present economically and environmentally attractive reactions, they are challenged by high operating temperatures, undesirable side reactions, catalyst deactivation, and in some cases, the use of toxic materials like Cr-based catalysts. Thus, there is a growing interest in developing selective and non-toxic catalysts for these reactions.

Supported single-atom catalysts (SACs) and subnanometer metal clusters offer a promising solution by combining the high selectivity of homogeneous catalysts with the thermal stability of heterogeneous systems. These atomically dispersed catalysts exhibit unique electronic properties due to strong metal-support interactions, which can be fine-tuned via support composition or defects. However, their structural heterogeneity and dynamic behavior under reaction conditions make experimental characterization difficult. This thesis addresses these challenges by developing multiscale computational frameworks that systematically explore the active site landscape and link atomic-scale structure to experimental catalytic performance.

In Chapter 2, we investigate the EDH mechanism on Co/SiO<sub>2</sub> catalysts using electronic structure calculations and microkinetic modeling. The catalyst comprises paramagnetic  $Co^{2+}$  sites anchored on an amorphous silica support. Both monomeric ( $Co^{2+}$ ) and dimeric ( $-Co^{2+}-O-Co^{2+}-$ ) sites are considered to assess the influence of site nuclearity on catalytic activity. The dominant reaction mechanism is shown to involve spin-crossing, and a methodology is developed to incorporate the probability of spin-crossing events into the microkinetic model. Chapters 3 and 4 expand this framework to examine how cobalt's coordination environment and crystallinity of the support influence reactivity. In Chapter 3, an ensemble of  $Co^{2+}$  sites is generated from an amorphous SiO<sub>2</sub> surface, and a workflow is developed to compute site-averaged apparent activation energies for comparison with experimental kinetics. This analysis also reveals key geometric descriptors of the catalytic sites that govern activity. Chapter 4 extends the mechanistic study to Co/BEA catalysts, in collaboration with experimentalists, to explore the role of support defects and crystallinity in modulating EDH activity.

Chapter 5 focuses on active site heterogeneity in Pt-CHA catalysts for EDH. Ab initio molecular dynamics simulations are employed to identify stable monomeric and dimeric Pt motifs associated with framework Sn<sup>4+</sup> and silanol defects. The coordination environments that disperse Pt atoms are identified, and the interaction of Pt with the zeolite framework is analyzed using electronic structure calculations. A kinetic ranking of the active sites is constructed to assess their relative catalytic relevance. Chapter 6 investigates metal-support interactions in atomically dispersed Ni on ceria–zirconia mixed oxides (CZO), a catalyst known for high activity and coke resistance in the DRM reaction. Using electronic structure methods and statistical thermodynamics, the influence of reaction conditions on support reducibility and Ni stability is elucidated.

In summary, this thesis demonstrates the critical role of atomistic modeling in accessing catalytic length and timescales that are challenging to probe experimentally, thereby bridging the gap between experimental observations and fundamental mechanistic understanding.