STEVENS
INSTITUTE OF TECHNOLOGY
1870

Ph.D. DISSERTATION DEFENSE

Candidate:	Shuqiao Wang
Degree:	Doctor of Philosophy
School/Department:	Charles V. Schaefer, Jr. School of Engineering and Science / Department of Chemical Engineering and Materials Science
Date:	Thursday, May 1st, 2025
Time/Location:	2:00 PM EST / Babbio 310
Title:	Dopant Effects on the Catalytic Performance of Ethane Oxidative Dehydrogenation over NiO-Based Catalysts
Chairperson:	**Dr. Alyssa Hensley**, Department of Chemical Engineering and Materials Science, Charles V. Schaefer, Jr. School of Engineering and Science
Committee Members:	**Dr. Jae Chul Kim**, Department of Chemical Engineering and Materials Science, Charles V. Schaefer, Jr. School of Engineering and Science **Dr. Pin-Kuang Lai**, Department of Chemical Engineering and Materials Science, Charles V. Schaefer, Jr. School of Engineering and Science **Dr. Jacob Gissinger**, Department of Chemical Engineering and Materials Science, Charles V. Schaefer, Jr. School of Engineering and Science **Dr. Fanglin Che**, Department of Chemical Engineering, Francis College of Engineering, University of Massachusetts Lowell

ABSTRACT

Light olefins are essential chemical building blocks in the petrochemical industry, with ethylene serving as a key feedstock for producing polyethylene, ethylene oxide, and other important plastics and intermediates. Conventional ethylene production via steam cracking is energy-intensive with high carbon intensity. Ethane oxidative dehydrogenation (EODH) is a promising catalytic alternative to reduce operating temperatures and hamper side reactions. Despite the advantages, the formation of carbon dioxide as a byproduct remains a major obstacle for the broad industrial application of EODH, highlighting the need for effective catalysts with improved catalytic performance. Nickel oxide (NiO)-based catalysts have demonstrated potential for EODH at relatively low temperatures, with dopant incorporation (forming M-NiO) leading to enhanced ethylene selectivity. However, the nanoscale, mechanistic role of dopants remains unclear due to limited understanding of active surface structures and dopant interactions with ethane-derived intermediates.

Here, I address the challenges in M-NiO catalyst design for EODH through a comprehensive, multiscale modeling framework. Using density functional theory (DFT) and *ab initio* thermodynamics, dominant M-NiO surface structures are identified under realistic EODH conditions. A series of high-valence dopants (Al, Mo, Nb, Sn, Ti, V, W, Zr) are investigated on both (100) and (110) NiO facets, with consideration of surface/subsurface doping, various defect types (Ni/O vacancies in the surface/subsurface), and surface oxygen species (O*, O_2*). Results show that dopants preferentially bind adsorbed oxygen species due to their strong oxophilicity, indicating the formation of a new, stable active site with doping. To evaluate catalytic mechanisms, potential energy surfaces (PES) from ethane to ethylene versus CO_2 are first screened on pure NiO(100) surfaces, revealing that CH_3CH_2* binds the catalyst surface too weakly—critical limitations that can be tackled by dopant effects. A comparative study on Nb-NiO(100) shows that the issue with weak CH_3CH_2* adsorption remains while the deeper dehydrogenation pathway to CH_2CH* is suppressed. Additionally, a microkinetic model (MKM) is constructed, further allowing the identification of rate-determining step and surface coverage examination during EODH. Finally, a systematic screening across all M-NiO(100) systems is performed to evaluate the adsorption energies of specific EODH intermediates. A descriptor-based analysis identified dopant influence on selectivity-determining steps, enabling predictive insights for rational catalyst design.

This work advances fundamental understanding of dopant effects on EODH selectivity related mechanisms on M-NiO from a nanoscale perspective and provides a dopant-by-design strategy to accelerate the discovery of future NiO-based EODH catalysts.