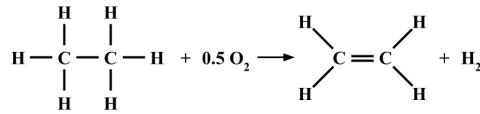
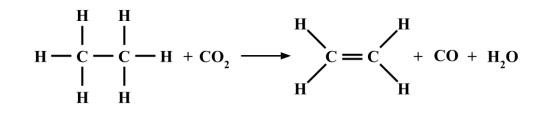


Cobalt Molybdate Catalyst

Ethane Dehydrogenation – Reaction Schemes



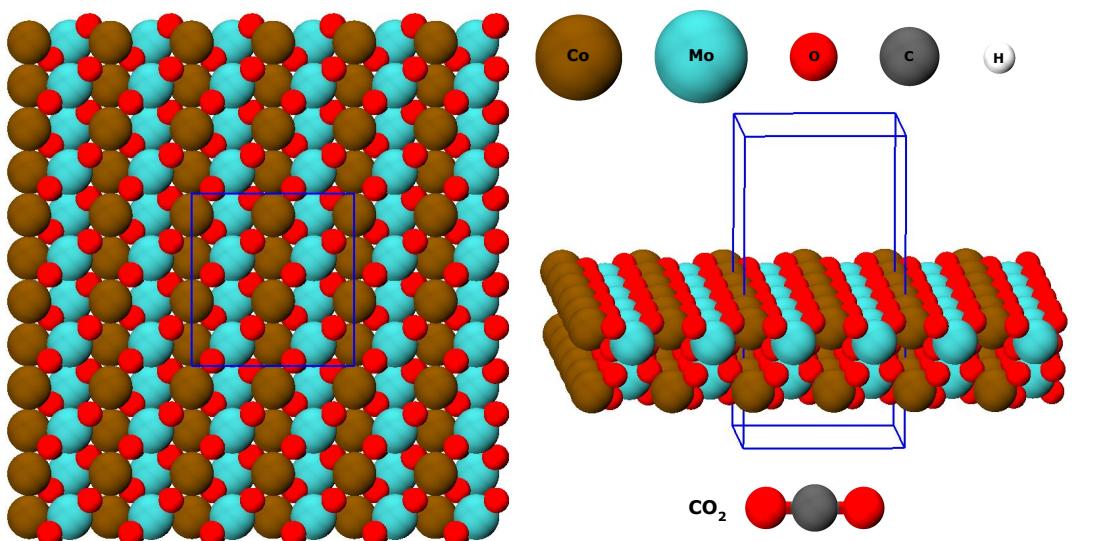
Scheme 1. Ethane Dehydrogenation using O_2 oxidant



Scheme 2. Ethane Dehydrogenation using CO_2 oxidant

Advances in the chemical processing industry have led to increased use of small alkanes over traditional oils. The dehydrogenation of ethane is critical for the production of ethylene, which can be used to synthesize different chemicals and fuels. Generally, oxygen is reacted with ethane to produce ethylene and water (Scheme 1). However, ethane can be reacted with carbon dioxide instead of oxygen to create ethylene, carbon monoxide, and water (Scheme 2). There are two important benefits of using the right pathway instead of the left. The first benefit is that carbon dioxide only reacts with the subsequent hydrogen, which can improve selectivity for dehydrogenation and prevent ethane conversion to undesired products. The next benefit is that such processes also utilize carbon dioxide, which may help reduce emissions in ethylene production. One of the challenges of this process is the significant energy input required for dehydrogenation. The goal of this project was to understand the mechanisms of such carbon dioxide assisted dehydrogenation reactions on cobalt molybdate catalysts using density functional theory (DFT) based molecular simulation.

Cobalt Molybdate – CoMoO_4 (010)



Cobalt molybdate was chosen as a catalyst in this reaction (Scheme 2) because it was found to be promising in experimental studies. Catalysts can lower the activation energy for a reaction by either orienting the reacting particles in such a way that successful collisions are more likely or reacting with the reactants to form an intermediate that requires lower energy to form the product. The molecular structure of cobalt molybdate is shown above.

References

Ridha, T.; Li, Y.; Gencen, E.; Siirila, J. J.; Miller, J. T.; Ribeiro, F. H.; Agrawal, R., Valorization of Shale Gas Condensate to Liquid Hydrocarbons through Catalytic Dehydrogenation and Oligomerization. 2018, 6 (9), 139.

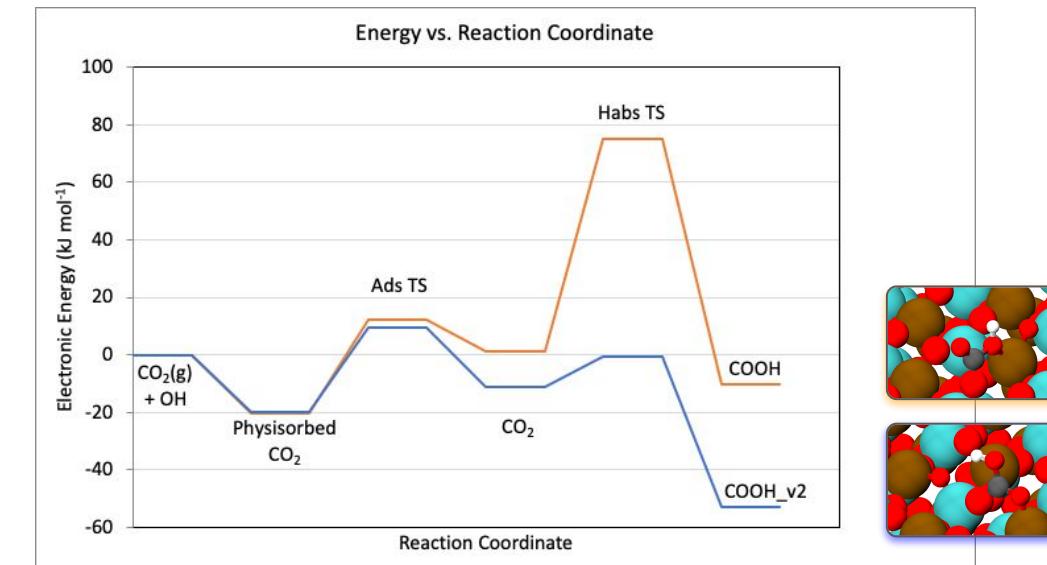
Mimura, N.; Okamoto, M.; Yamashita, H.; Oyama, S. T.; Murata, K., Oxidative Dehydrogenation of Ethane over Cr/ZSM-5 Catalysts Using CO_2 as an Oxidant. The Journal of Physical Chemistry B 2006, 110 (43), 21764-21770.

Yao, S.; Yan, B.; Jiang, Z.; Liu, Z.; Wu, Q.; Lee, J. H.; Chen, J. G., Combining CO_2 Reduction with Ethane Oxidative Dehydrogenation by Oxygen-Modification of Molybdenum Carbide. ACS Catalysis 2018, 8 (6), 5374-5381.

Altarawneh, I.S., Rawadih, S.E., Batiba, M.A., Al-Makhadmeh, I.A., Al-Shawesh, M.A. and Altarawneh, M.K., 2018. Structures and thermodynamic stability of cobalt molybdenum oxide (CoMoO_4 -II). Surface Science, 677, pp.52-59.

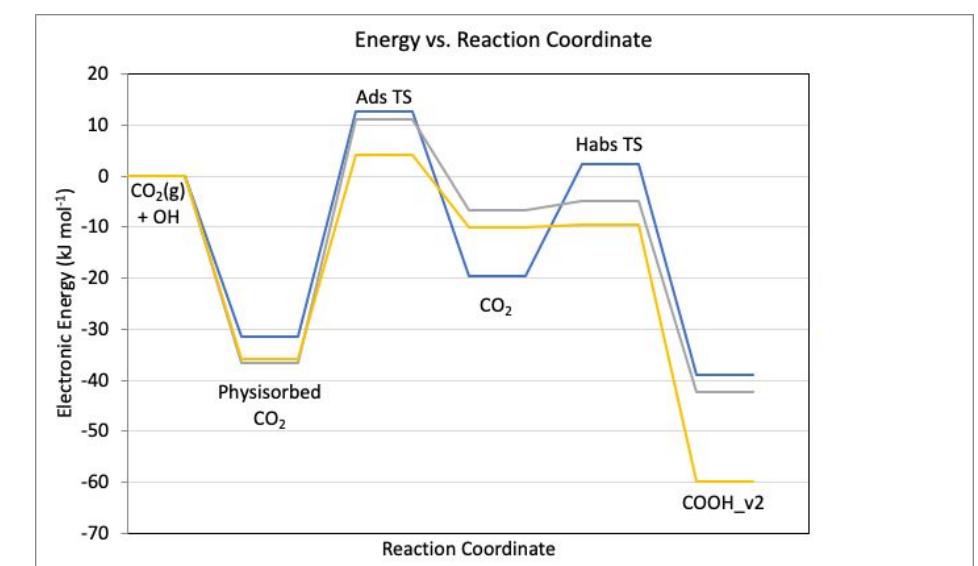
Jayson Pinals, Tufts University

Energies of Mechanisms – Results Comparison



This figure shows the electronic energy of the six states for both mechanisms: the first mechanism in orange and the second mechanism in blue. The energy of each state was found using VASP, which is a package for performing density functional theory (DFT) calculations. Linux was used to edit and submit VASP calculations in the Tufts HPC Research Cluster and Stampede2 Supercomputer was used to run the VASP calculations. In this figure, a state with lower electronic energy is more stable. The COOH_{v2} resulting structure is more stable than that for COOH . There is about a 40% decrease in energy change from the first mechanism's final structure to the second's. More interestingly, the second transition state for the second mechanism is much more stable; there is an 86% decrease in energy change from the first mechanism's transition state to the second's. This means that the second mechanism requires less energy to reach the second transition state.

Higher Hydrogen Coverage – Mechanism_v2 Comparison



This figure shows the energies of the second pathway with added hydrogen coverage on the surface of the catalyst. Each of the colors represents a different location of one additional hydrogen on the surface. This is meant to explain how the energy of the system is affected when there are two hydrogens on the surface. These results will be used to model and calculate the electronic energies of the final steps of the overall ethane dehydrogenation reaction.

Acknowledgments

Prashant Deshlahra, Chemical and Biological Engineering at Tufts University

Cathy Chin, Chemical Engineering and Applied Chemistry at University of Toronto