

Towards Atomistic Understanding of CO₂ Reduction to Fuels over Carbon-Based Metal-Free Electrocatalysts

PRF# 58410-DNI5

PI: Vitaly Alexandrov

Affiliation: University of Nebraska-Lincoln

Overview

Direct production of methanol and complex oxygenates (C₂₊ products) from carbon dioxide (CO₂) and hydrogen has been exalted as a valuable means to reuse CO₂ as energy-storing and valued-added chemicals. The goal of this project is to develop an atomistic understanding of the CO₂ reduction process to produce fuels over a variety of catalysts. The competing process of electrocatalytic water splitting is of great interest too.

Results

To examine reaction mechanisms of CO₂ hydrogenation, we have focused on the catalyst comprised of CeO_{2-x} as a support and a Ru nanoparticle. By employing the density-functional-theory (DFT) calculations, we first analyzed the stability of Ru₁₀ clusters of different shapes on the CeO₂(110) surface and identified the most energetically favorable positions of adsorbed hydrogen and CO₂ species (see Fig. 1).

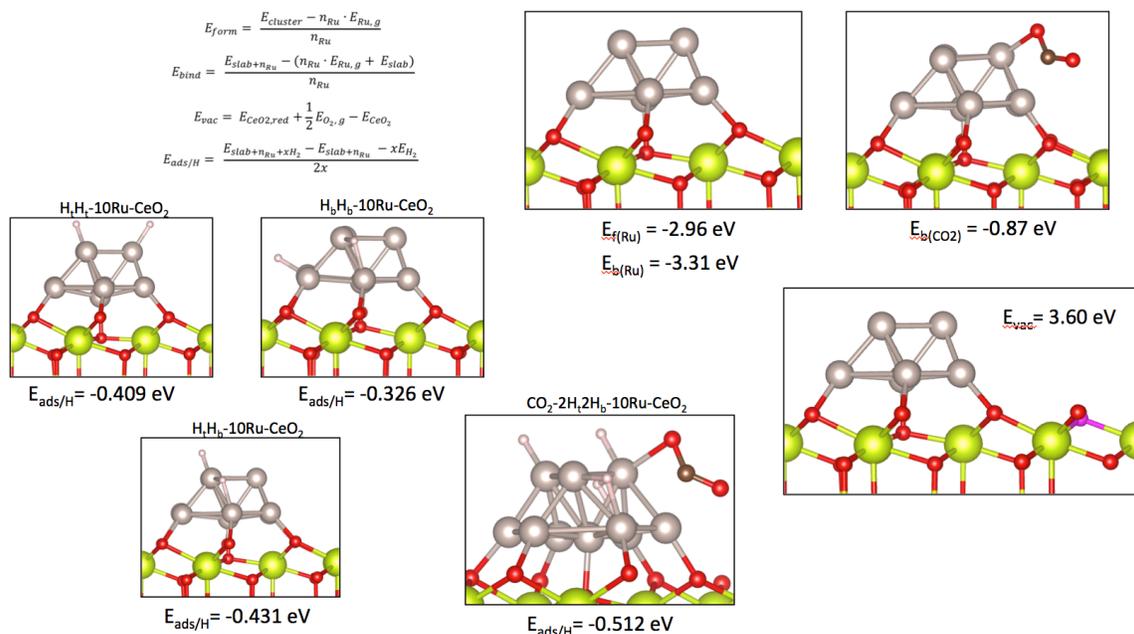


Figure 1. DFT energetics of species (H and CO₂) adsorption at the Ru₁₀/CeO₂ catalyst.

After this first step, we have proceeded to study the energetics of CO₂ hydrogenation at the CeO₂ interface (Fig. 2). This is to reveal the reaction pathways and identify factors that can help drive the formation of desired oxygenates. Once Ru/CeO₂ system is examined, we will use the gained knowledge to commence simulations with cheaper metals such as Ni, which turned out to be more challenging due to their magnetic properties. Overall, the obtained computational insights are to be tested in experiments through our collaboration with a UNL chemistry professor. We hope that our computational-experimental results collectively will guide the synthesis of selective catalytic systems for CO₂ conversion to C₂₊ products.

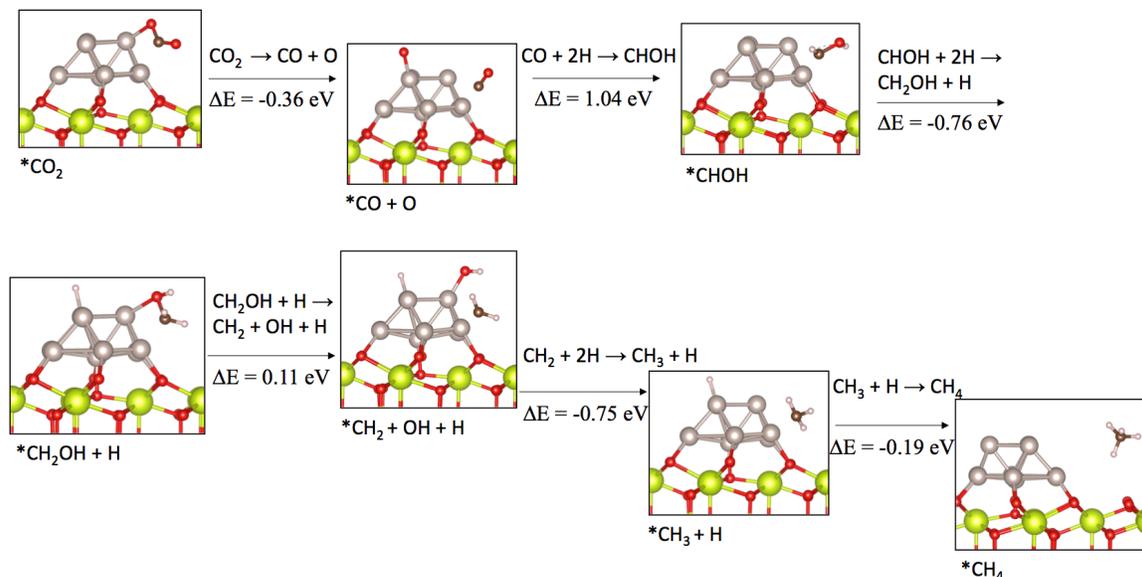


Figure 2. The computed reactions of CO_2 hydrogenation with the corresponding energies.

One of the important parameters that can affect CO_2 reactivity is the presence of oxygen vacancies in CeO_2 . For example, it can help create surface hydroxyls that may hydrogenate adsorbed CO_2 . We are currently investigating the role of oxygen vacancies (see Fig. 3) in the interfacial charge transfer and overall reaction mechanism.

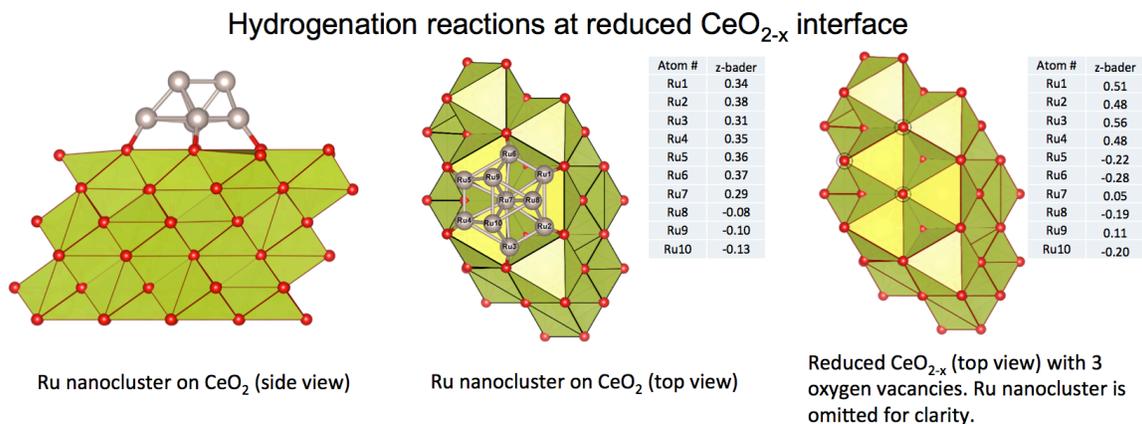


Figure 3. Modeling reduced CeO_{2-x} support for subsequent reactivity studies.

Career development

This ACS PRF grant has supported the stipend of one female graduate student (Alexandra Zagalskaya). Alexandra has presented her work as a poster at the Telluride Summer School on Theoretical Chemistry in summer 2019. She has also given a presentation for undergraduate students from other universities during the Conference for Undergraduate Women in Physical Sciences at UNL (fall 2018) sharing her graduate school experience and promoting STEM careers among women. The support from this grant has also enabled the PI to give an invited talk at the last ACS meeting (fall 2019). Overall, the grant has been instrumental for developing the PI's career as an assistant professor.