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Coaches	**Supervisor(s)**	**Funding**
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Dopant Effects on CO_2 Hydrogenation to Methanol over In_2O_3: Mechanistic Insights into Activity and Surface Interactions

Aim

Analysing effect of the dopant on catalyst activity and surface Interactions on the CO_2 hydrogenation to methanol over Indium oxide catalysts using:

1. Density functional theory (DFT) calculations
2. Machine Learning
3. Microkinetic modelling

Justification

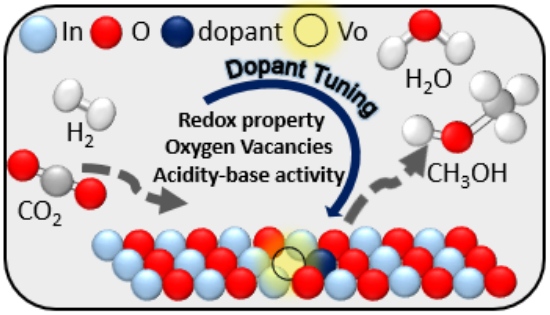

Figure 1. Illustration of the CO_2 to methanol reaction over In_2O_3 catalyst.

Electrification is a key strategy in the EU Green Deal. Direct electrification is however not always feasible, and converting H_2 and CO_2 into methanol offers a cost-effective and scalable alternative to store renewable energy and convert CO_2 into chemical building blocks. Methanol is compatible with existing infrastructure for transport, storage, and industrial use.

In_2O_3 exhibits high theoretical activity and selectivity for CO_2 hydrogenation to methanol, with no prior reports of a single oxide achieving such performance.[1] Atomic metal and non-metal dopants influence catalytic activity by modifying the electronic structure. Resulting differences in Lewis acidity, redox properties, hydrogen activation, and spillover effects are proposed to be responsible for the enhanced perfromance.[2-4] Catalyst structure, surface coverages and ease of oxygen vacancy creation at reaction conditions significantly influence catalyst performance. However, the reverse Mars–van Krevelen (MvK) mechanism is often overlooked in CO_2 hydrogenation but could play a crucial role in oxygen vacancy (Vo)-mediated catalysis. This study aims to investigate how Vo formation, migration, and regeneration influence CO_2 activation and selectivity on In_2O_3-based catalysts. Combining DFT calculations with microkinetic modeling, we seek to establish the significance of this novel mechanism in redox cycling and hydrogenation pathways, providing new insights into catalyst design. Understanding how surface properties influence reactivity requires integrating molecular modeling with microkinetic simulations to bridge theoretical insights with experimental observations.

In this proposal, we aim to bridge the gap between computational models and realistic catalyst behavior by leveraging advanced computational modeling, machine learning (ML), and compare with experimental data obtained at the LCT. We will systematically explore how various dopants affect surface coverages, catalyst reconstructions, and active sites influence CO_2 hydrogenation to methanol.

Program

1. Literature review: Experimental and theoretical studies on CO_2 hydrogenation to methanol over In_2O_3-based catalysts, with a focus on selectivity and active sites.
2. Computational surface science studies to investigate the synergy between dopant-In_2O_3 and understanding roles of various surface sites and species.
3. Using Machine Learning Potentials to expedite understanding of surface evolution and activity.
4. Microkinetic modeling to evaluate the effect of realistic surface coverages on activity and selectivity.

References

1. K. Sun et al., *J. CO_2 Util.*, 2015, **12**, 1.
2. F. Cannizzaro et al., *ACS Catal*., 2023, **13**, 1875.
3. Y. Yang et al., *ACS Catal.*, 2023, **13**, 6154.
4. L. Liu et al., *ACS Catal.*, 2023, **13**, 15730.

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