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## Computational investigation of the structure and activity of supported Ni- and Co-based catalysts

### Aim

Analysis of the surface structure and activity of Ni-based catalysts in the CO<sub>2</sub> hydrogenation to methane (and olefins) using:

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

### Justification

Recently, the European Commission presented its Green Deal to become the 'first climate-neutral continent'. Electrification of the economy is a key component of the Green Deal, but direct electrification is not the best option for many sectors. One of the routes explores the use of hydrogen as a possible energy carrier, but high transportation and storage costs are associated with hydrogen. Therefore, routes to convert hydrogen into molecules that are compatible with the current infrastructure such as methane or other valuable chemicals, like olefins, are highly desirable.

Nickel is often used as a catalyst for the methanation of CO<sub>x</sub>, while cobalt is an excellent FT catalyst. First-principles modelling, such as DFT, can be employed to understand the mechanism better. In a first part, an existing microkinetic model will be used, where the influence of temperature, pressure and feed composition will be investigated.

In the next stage, the role of the support and promoters will be investigated using DFT calculations. Ceria-Zirconia supports have been proven to boost CO<sub>2</sub> methanation for Co-based catalysts<sup>1, 2</sup>, while TiO<sub>x</sub> supports tune the selectivity towards C<sub>2+</sub> hydrocarbons<sup>3, 4</sup>. Modelling of the effects of the support and promoters has been limited, leaving a knowledge gap in our understanding of the reaction mechanism. Currently, catalysts are assumed to be metallic under reaction conditions, but the shift to CO<sub>2</sub>-rich feeds can alter the stability of oxides and might impact the stability of active sites. Additionally, the support-metal interface, the support itself are promising alternative active sites. Promoters on the other hand can also significantly affect reactivity. These new insights can be implemented in the microkinetic model and further analyzed.

### Program

1. Literature review: role of the support and promoters on CO<sub>2</sub> methanation over Ni and Co.
2. Microkinetic modelling of the CO<sub>2</sub> methanation reaction on Ni- and Co-based catalysts.
3. Computational surface science studies to investigate the effect of the support and promoters on the active sites and reactivity of Ni- and Co-based catalysts.
4. Expansion of the microkinetic model.

### References

1. A. Parastaev, et al., *Nat. Catal.*, 2020, **3**, 526-533.
2. A. Parastaev, et al., *Nat. Catal.*, 2022, **5**, 1051-1060.
3. I. C. t. Have, et al., *Nat. Commun.*, 2022, **13**, 324.
4. M. Xu, et al., *Nat. Commun.*, 2022, **13**, 6720.

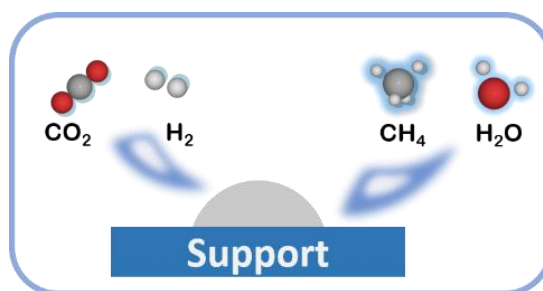


Figure 1. Illustration of the CO<sub>2</sub> methanation reaction over supported Ni- and Co-based catalysts.