

Conversion of CO₂ Within Sustainable Process Industry Through Resource and Energy Efficiency

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Abstract The Laboratory of Catalysis and Chemical Reaction Engineering (LCCRE) within the National Institute of Chemistry, Slovenia, is alongside several European academic and industrial partners involved in the development of innovative green chemical production technologies in an industrially-relevant environment by increasing the overall resource efficiency and energy intensity, and by decreasing the greenhouse gas emissions into the environment. The mentioned research and innovation efforts are joined under the SPIRE initiative within the Horizon 2020 Framework Programme.

Keywords: • CO₂ Conversion • DFT • KMC • CFD • multiscale modelling •

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1 Introduction

The MefCO₂ (Synthesis of Methanol from Captured Carbon Dioxide Using Surplus Electricity) and FReSMe (From Residual Steel Gases to Methanol) projects are aimed at an increase of renewable energy usage and a decrease of CO₂ emissions, which are important European strategic objectives. Carbon dioxide, a greenhouse gas, which would normally be emitted into the atmosphere, is captured and converted to methanol with hydrogen, which is produced by water electrolysis. The electricity, used for electrolysis, is obtained from the surplus electricity at the peaks of its generation from renewable resources (wind, solar, etc.), simultaneously stabilizing the electrical grid. The product, methanol, is a widely-useable platform chemical and a precursor for further synthesis.

A comprehensive list of theoretical calculations for methanol synthesis was carried out to better understand the kinetics and mechanism of the reaction on a complex catalyst. To study kinetics of the catalysed reaction, a crystal structure was constructed that mirrored the actual catalyst structure, based on existing literature data and our experimental techniques. We studied detailed kinetics on four catalyst combinations (Zn₃O₃/Cu, Cr₃O₃/Cu, Fe₃O₃/Cu, and Mg₃O₃/Cu), which had not been done in such detail before. A thorough reaction pathway network was put together and investigated using density functional theory (DFT), including less frequently encountered intermediates and reactions on side pathways. We calculated reaction rates at different temperatures and pressures. All possible elementary reaction steps were considered.

2 Operational laboratory-scale reaction models

2.1 Density functional theory modelling

Density functional theory (DFT) calculations were carried out with the program suite Quantum Espresso 5.4 [1], which uses PWscf code to calculate the electronic structure of periodic atomic structure. For visualization of structures, an open-source tool XCrysDen was used [2]. As the best compromise between accuracy and computational cost, Perdew-Burke-Ernzerhof (PBE) functional was selected [3,4]. Ultrasoft pseudopotentials from scalar-relativistic calculations were used. To account for insufficient description of van der Waals interactions by DFT methods, a modified semi-empirical Grimme dispersion correction was

included [5]. Convergence testing showed that the kinetic energy cut-off of 300 eV and wavefunction cutoff of 2400 eV sufficed to obtain well converged results. Metallic nature of the catalyst was taken into account by using Gaussian spreading of width 0.1 Ry for Brillouin zone integration. It was sampled on a Monkhorst-Pack mesh with 8 x 8 x 1 points [6]. Convergence threshold of 10⁻⁸ Ry for self-consistent cycles was selected. For geometric optimisation of adsorbates, residual forces were required to drop below 10⁻³ Ry/au and energy change per step below 10⁻⁴ Ry. For gaseous species calculations, a large (25 × 25 × 25 Å) cubic cell was used. As there is no periodicity to account for, Brillouin zone was sampled at a single point (Γ) and no dipole correction was used. To seek for the transition states, nudge elastic band (NEB) method was used. After preliminary identification of the transition state structure, it was determined with climbing image approach until forces orthogonal to the reaction path dropped below 0.05 eV/Å [7,8]. Vibrational analysis was carried out to ensure that each transition state structure had exactly one imaginary frequency, corresponding to the movement along the reaction coordinate. For adsorbed species, zero-point energy (ZPE) correction was calculated from the vibrational component only, perturbing only adsorbate atoms

$$\Delta E_{ZPE} = \sum_i^{3N} \frac{h\nu_i}{2}. \quad (1)$$

Adsorption energies of reactants, intermediates and products were calculated as

$$\Delta E_{ads} = E_{species+catalyst} - E_{catalyst} - E_{species} + \Delta E_{ZPE}. \quad (2)$$

Reaction barrier (E_A , activation energy) and reaction energy (ΔE) for each elementary step were calculated in a standard fashion as

$$E_A = E_{TS} - E_{reactant} \quad (3)$$

and

$$\Delta E = E_{product} - E_{reactant}. \quad (4)$$

This allowed us to obtain reaction rates as

$$k_{fwd} = \frac{k_B T}{h} \frac{q_{vib,TS}}{q_{vib,IS}} e^{-\frac{E_A}{k_B T}} \quad (5)$$

where k_B denotes Boltzmann constant, T absolute temperature, h Planck constant and q_{vib} vibrational partition function, which is in turn estimated from the real vibrational contributions only (as the imaginary mode along the reaction coordinate is factored out in transition state theory) as

$$q = \prod_i^{3N} \frac{1}{1 - e^{-\frac{h\nu_i}{k_B T}}}, \quad (6)$$

Equilibrium constants are obtained from

$$K = \frac{k_{fwd}}{k_{bwd}} = e^{-\frac{\Delta E}{k_B T}}. \quad (7)$$

and allow us to determine the rates for the reverse reactions

$$K = \frac{k_{fwd}}{k_{bwd}} = \frac{q_{vib*}}{q_{vib} q_{rot} q_{trans,g}} = e^{-\frac{\Delta E_{ads}}{k_B T}}, \quad (8)$$

For adsorbed hydrogen atoms, surface diffusion was explicitly taken into account as an elementary reaction, when hydrogen migrates from one fcc site on Cu to the adjacent one.

Kinetic constants for adsorption and desorption are obtained from the collision theory. Rate of adsorption can be evaluated if we assume that the sticking probability equals unity as

$$k_{ads} = \frac{1}{N_0 \sqrt{2\pi m k_B T}} \quad (9)$$

where N_0 denotes the number of reaction sites per catalyst as $1.9 \cdot 10^{17} \text{ m}^{-2}$ and m the mass of a molecule. For desorption rate, one calculates the equilibrium constant and by taking into account vibrational, rotational and translational components of the partition function for gaseous species.

$$K = \frac{k_{ads}}{k_{des}} = \frac{q_{vib,ads}}{q_{vib,g}q_{rot}q_{trans}} \exp\left(-\frac{E_{ads}}{k_B T}\right) \quad (10)$$

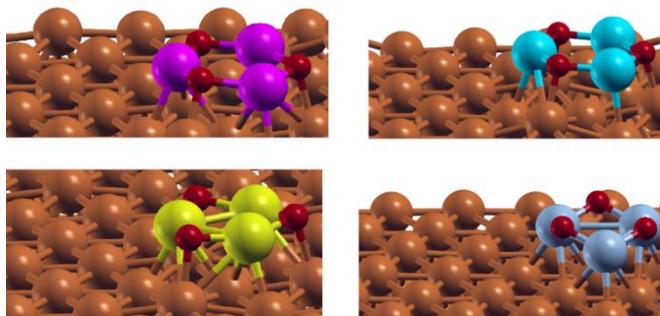


Figure 2: Modelled active site of the M₃O₃/Cu catalyst (from top left clockwise M: Zn, Mg, Cr, Fe) consists of a M₃O₃ deposited atop of Cu(111) plane. Reactions proceed at the interphase boundary.

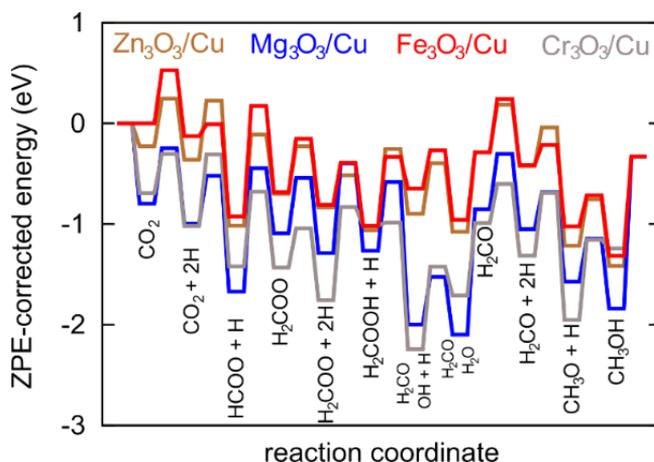


Figure 2: Potential energy surface for the most probable reaction route on all four studied catalysts. Note that CO₂ does not bind to Fe₃O₃/Cu catalyst, effectively making the reaction follow the Eley-Rideal mechanism.

2.2 Kinetic Monte Carlo (KMC) simulations

Using the graph-theoretical KMC software package Zacros, we simulate methanol (CH₃OH) synthesis from CO₂ hydrogenation. We focus on theoretically modelled catalysts, in particular the Cu(111) and the commercial-like Cu/metal oxide catalysts (Zn,Cr,Fe,Mg)₃O₃/Cu. We study methanol synthesis via formate (HCOO) and hydrocarboxyl (COOH) reaction path, but

also include H_2O effects and reverse water-gas shift (RWGS) reaction path. The dependence of conversion, selectivity, and the rate of desorbed bulk CH_3OH production upon operating process conditions, primarily temperature and pressure, was examined. Furthermore, KMC simulations provide the detailed surface coverage and elementary steps' event frequency, to study the catalytic performance in temporal domain [9]. The results are qualitatively well comparable with the available experimental data for heterogeneous copper-based materials. This demonstrates that an accurate evaluation of ab initio theoretical research is crucial, especially upon paralleling them to experimental reactor concentrations.

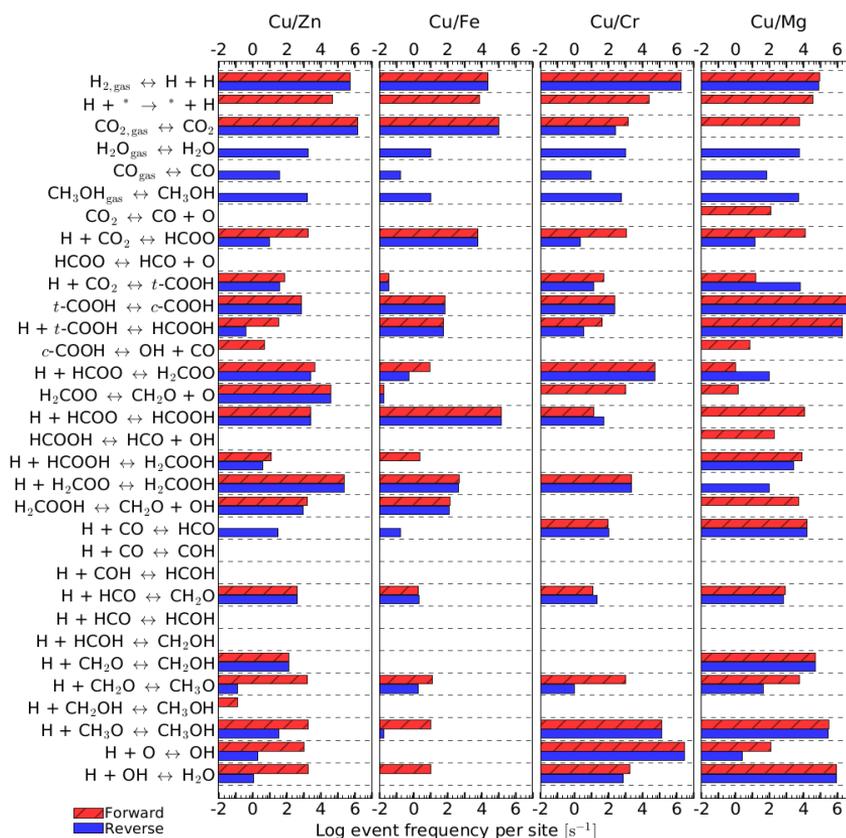


Figure 2: Elementary step frequency for the case of $T = 500$ K and $P = 40$ bar, for all 4 investigated catalysts ($\text{M}_3\text{O}_3/\text{Cu}$ catalysts, M being Zn, Cr, Fe, or Mg). Red steps indicate forward reactions, while blue ones indicate reverse reactions. From [10].

2.3 Fluid dynamics and transport phenomena (computational fluid dynamics – CFD)

In contrast to empirical correlation (EC), computational fluid dynamics (CFD) acknowledges specific vessel geometry, where local physical and chemical phenomena, contributing to apparent catalytic turnover, prevail. Presently, EC and CFD were compared considering the pressure drop predictions within the packed bed columns for spherical, cylindrical, trilobe and quadrilobe particle packing. 52 configurations were simulated and the estimations within EC validity range margins were in agreement with CFD (< 15%), while in extremes (non-negligible entrance and exit patterns), a 70% deviation could be exceeded. Furthermore, boundary wall effects were found to be dependent on the stacked pellet shape and orientation, and did not necessarily lead to an increase of viscous friction loss, relative to the infinitely wide systems, for the column-to-particle diameter ratios, lower than 10, which is contradictory to non-mechanistic relationship models. While the induced pressure difference within realistic fixed beds is elevated due to gas or liquid surface interaction and back-mixing, it can also be decreased by channelling/tunnelling, which is why the effective net influence should be analysed with CFD simulations, particularly in novel intensified and micronized processes, in which momentum, mass and heat transfer resistances are far from bulk medium continuity. Finally, new solver was developed which included surface catalytic reactions. On the bases of the Open Source Computational Fluid Dynamics (CFD) Toolbox OpenFoam we manipulate the reactingFoam solver which was developed for homogeneous reacting flows. To include heterogeneous catalytic reaction new dynamic boundary condition was written which was applied in the new solver called surfaceReactingFoam.

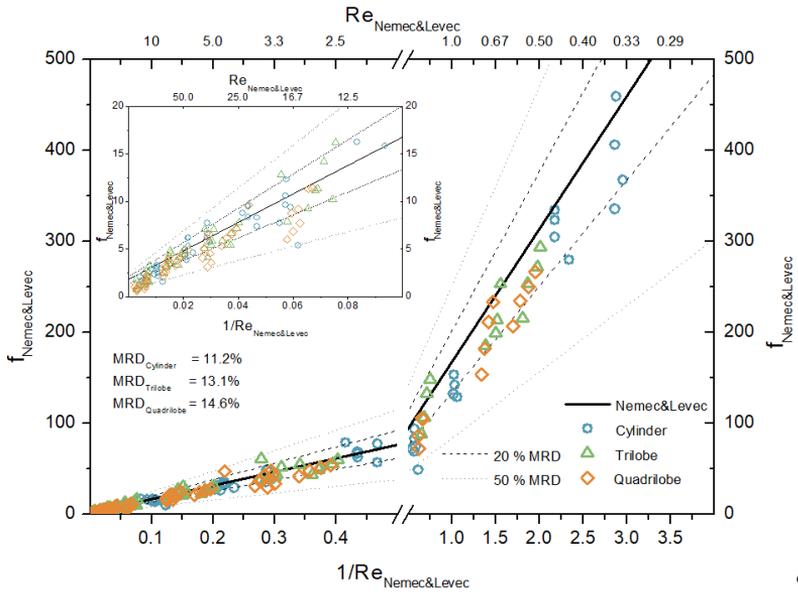


Figure 2: Modified friction factor predicted by CFD and Ergun correlation [11].

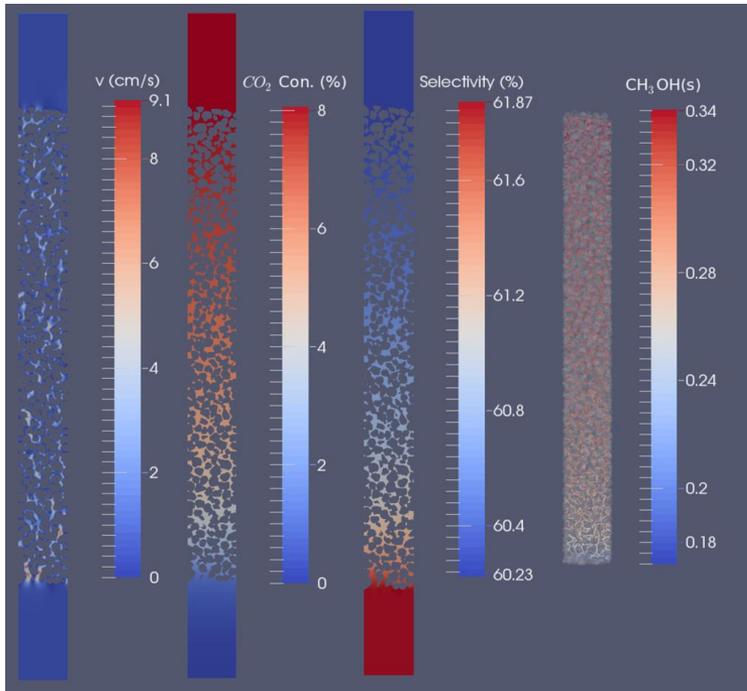


Figure 2: CO₂ hydrogenation to methanol at 220 °C – (left-right) – velocity field, CO₂ conversion, methanol selectivity and methanol coverage .

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