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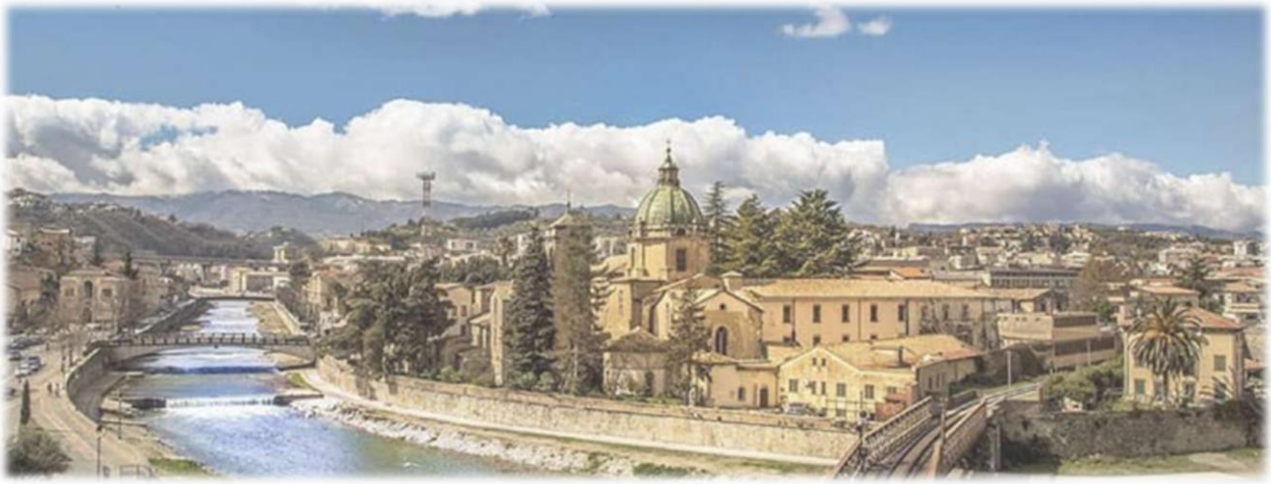

Università della Calabria, 1 e 2 dicembre 2025

Centro Congressi "Beniamino Andreatta"

Arcavacata di Rende (CS)

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FP5

Graph-based DFT microkinetic analysis of heterogeneous catalytic systems

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Graph theory originated and developed within a mathematical framework quite distinct from that of chemical kinetics, yet it can also prove to be a powerful tool in this field.[1] One of its most significant applications lies in the derivation of reaction rate expressions.

This work introduces, for the first time, a graph kinetic analysis (GKA) based on the combined use of graph theory and density functional theory (DFT), here referred to as DFT-GKA method. The preferential oxidation of carbon monoxide (CO-PROX) over a MnO_2–CeO_2 composite catalyst was selected as a case study.

The DFT-GKA method[2] begins with the identification of the fundamental catalytic cycles that compose a given overall catalytic mechanism. Using a custom filtering algorithm, the physically and chemically meaningful spanning tree graphs (Σ-Ts) — which connect all the nodes within a graph — and the coupling tree graphs (X-Ts) — which represent all the steps of a polycyclic system that do not belong to a given cycle but that intersect it within that system — are identified and selected.

These Σ-T and X-T graphs enable the evaluation of two kinetically significant aspects: Σ-Ts account for the effects of all possible chains of elementary steps involved in the overall mechanism, while X-Ts describe the influence of each step on cycles to which it does not belong.

For each selected graph, the probability of occurrence of every surface reaction event is evaluated based on the activation free energies computed by DFT. From these energy data, the rate constants of each elementary step are determined using the Eyring–Polanyi formalism, suitably adapted to include both reactions involving surface adsorbed species and those involving gas-phase adsorption. Finally, the reaction rate values associated with the reaction channels of interest are obtained.

Through the fully computational and theoretical derivation of the reaction rates for H_2O and CO_2 formation, the DFT-GKA approach has enabled the determination of kinetic and thermodynamic descriptors — activity, selectivity, surface population, apparent activation energy, and reaction order — for the polycyclic mechanism governing the PROX reaction on MnO_2–CeO_2. The results are in good agreement with experimental data[3,4] at low temperatures.
The computed descriptors show that, at low temperatures, the oxidative processes of CO and H_2 occur on distinct time scales, supporting the experimental evidence of their independence. At higher

temperatures, however, the increased surface population of hyper-oxygenated catalytic sites promotes H_2 oxidation, explaining the experimentally observed decrease in selectivity toward CO oxidation.
These findings demonstrate that the DFT-GKA method is already effective for the kinetic analysis of complex heterogeneous catalytic reactions under certain experimental conditions. Further development could provide a more comprehensive kinetic description and improve agreement with experimental data over a broader range of conditions.
For the PROX reaction, the availability of atomic oxygen diffusing from the cerium oxide support to the MnO_2 surface islands may play a key role at high temperatures. The DFT evaluation of the energetics associated with this diffusion process, once incorporated into the DFT-GKA framework, will allow for a refined mechanistic analysis of the system under such conditions.

Acknowledgements**:** *Authors acknowledge financial support under the National Recovery and Resilience Plan (PNRR), Mission 4, Component 2, Investment 1.1, Call for tender no. 104 published on 2.2.2022 by the Italian Ministry of University and Research (PRIN 2022), 2022EX89KF, funded by the European Union–NextGenerationEU–Project Title "An integrated environmental sustainable approach for the valorization of wet AGROindustrial wastes to bioMEThane" (AGROMET)–CUP B53D23005960006.*

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