

Introduction

Methane (CH₄) is a potent greenhouse gas, with a global warming potential approximately 28 times that of CO₂. The EU's CANMILK project aims to mitigate the emissions of barn CH₄ using plasma catalysis at low temperatures. For this, plasma-activated NO_x should help oxidize small quantities of CH₄ (≤ 1%) mixed in barn air. However, optimizing these systems is challenging due to the complexity of plasma-surface interactions and a lack of predictive kinetic models.

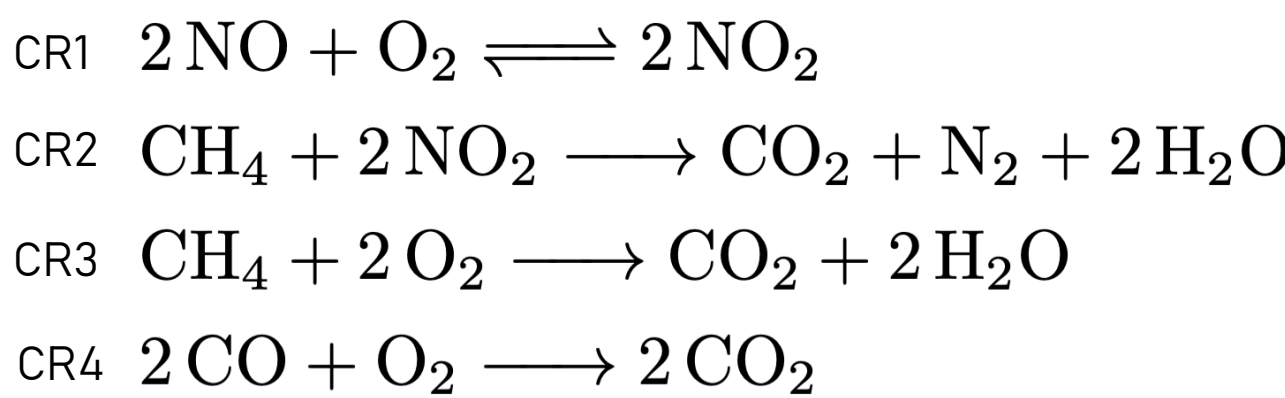
We develop a **kinetic model** from a data-rich proxy system: the plasma-catalytic removal of CH₄-NO_x from LNG engine exhaust, as studied by [1]. It consists of a **self-consistent Differential-Algebraic Equation (DAE) model**, based on a kinetic scheme assuming a single rate-limiting step per global reaction, with all other elementary reactions in a fast equilibrium regime.

This work establishes a first attempt to create a modelling tool that provides the foundation for designing reactors for the CANMILK project's methane abatement applications.

The Plasma-Catalytic System for Model Validation

The model is validated against the experimental work by [1], that investigates the removal of CH₄ and NO_x using a Dielectric Barrier Discharge (DBD) plasma reactor followed by a catalytic reactor. The catalyst consists of a physical mixture of 2% Cr-2% In/SSZ-13 (Si/Al=10) and Co/SSZ-12 (Si/Al = 10). The model addresses the catalytic kinetics.

Overall Reaction: The system is governed by four key global reactions.



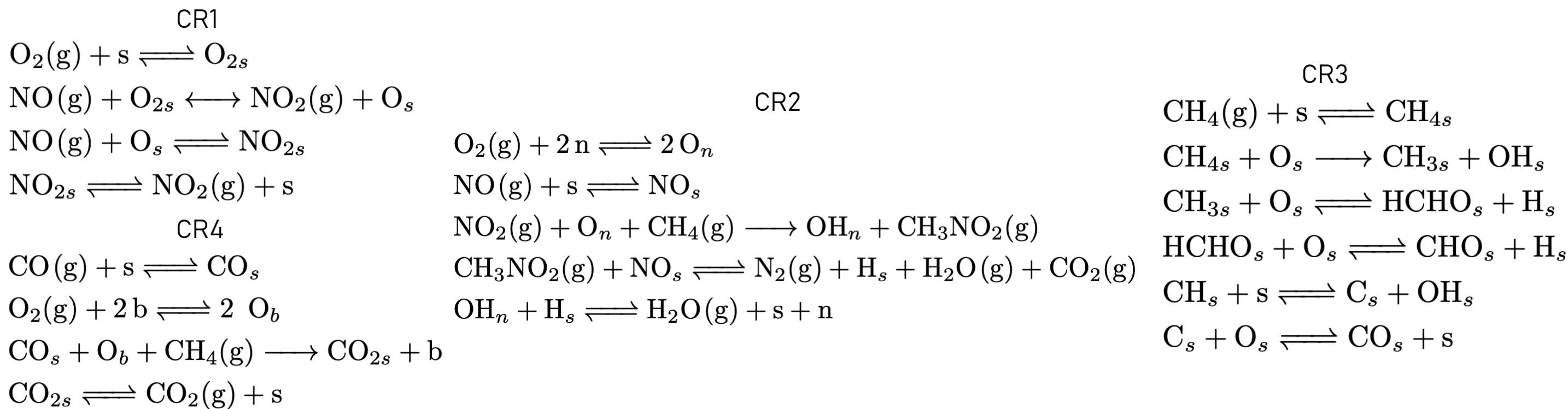
Our goal is to create a predictive model that captures the system's dynamics based on elementary reaction steps in a self-consistent way.

Model Formulation: A DAE Approach

The model is based on a detailed kinetic scheme [1], formulated as a system of Differential-Algebraic Equations (DAEs) that couple the gas-phase kinetics with the surface chemistry.

Key Assumptions:

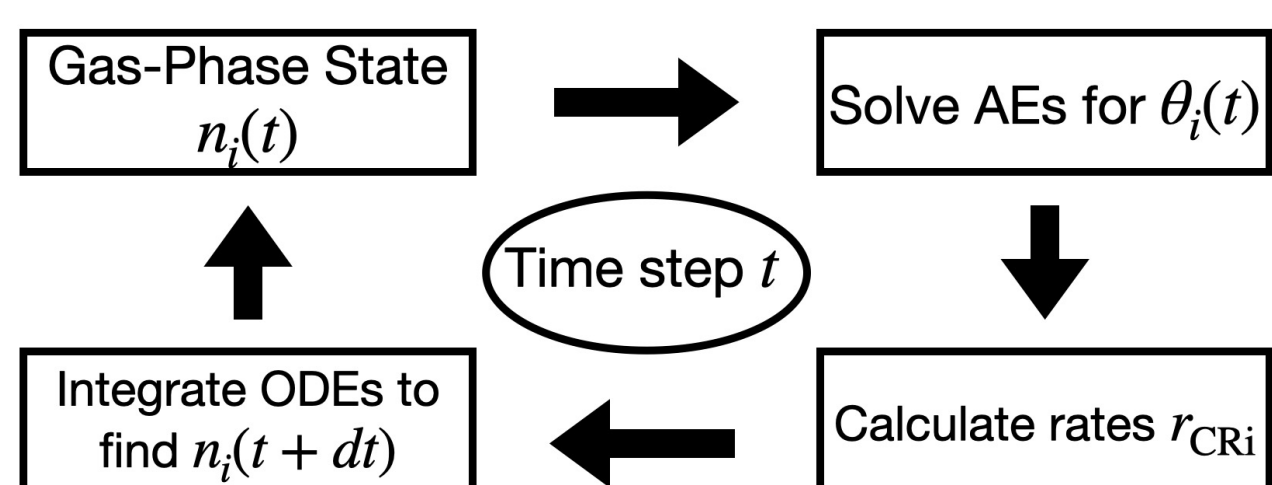
- Rate-Limiting Step** (→): For each of the four global reactions (CR1-CR4), one elementary step is assumed to be slow and rate-determining.
- Fast Equilibrium** (⇌): All other elementary steps are assumed to be in fast equilibrium regime.



s and n represent two different catalyst active sites and b indicates catalyst oxygen vacancies [1].

The DAE Structure: Coupling Gas and Surface

The set of assumptions creates a coupled system. The gas-phase concentrations evolve according to ODEs, but at any instant, the surface coverages are governed by a set of AEs.



The Algebraic Equations (AEs): Surface Chemistry at Equilibrium

The fast equilibrium assumption allows to express surface coverages (θ_i) as function of partial pressures (p_i) and the free surface variables (θ_{free}):

$$\theta_i = f_i(p_j(t), \theta_{\text{free}})$$

Example: For adsorbed oxygen, the coverage is given by: $\theta_{\text{O}_{2\text{s}}} = K_1 p_{\text{O}_2} \theta_\text{s}$

The Differential Part (ODEs): Gas-Phase Dynamics

The evolution of species densities is described by ODEs whose rates depend on the surface coverages calculated from the AEs [2,3].

Example: The change for CH₄ depends on the rates CR2 and CR3, which are themselves functions of the surface state θ :

$$\frac{d}{dt} [\text{CH}_4] = -r_{\text{CR2}}(\theta, p) - r_{\text{CR3}}(\theta, p)$$

with $r_{\text{CR2}} = k_{\text{CR2-3}} p_{\text{NO}_2} p_{\text{CH}_4} \theta_\text{n}$ and $r_{\text{CR3}} = k_{\text{CR3-2}} \theta_{\text{CH}_{4\text{s}}} \theta_{\text{O}_\text{s}}$. Here, the $k_{\text{CRi-j}}$ correspond to the reaction rate of the slow elementary step.

This structure creates the essential coupling between *fast* surface chemistry and the *slower* gas-phase evolution.

Constrained Optimization

Since the system of AEs for the s catalyst sites is under-determined, as we have more free variables ($\theta_{\text{free}} = [\theta_\text{s}, \theta_{\text{OH}_\text{s}}, \theta_{\text{CH}_\text{s}}]$) than constraints (site conservation), we have a non-unique solution. As a result, we consider a constrained optimization problem to find a unique and physically meaningful solution at each time step. We minimize the following objective function subjected to the AE constraints:

$$\min_{\theta_{\text{free}}} [\lambda \|\theta_{\text{free}}\|_2^2 + (1 - \lambda) \|\Delta\theta_{\text{free}}/\Delta t\|_2^2]$$

The first term corresponds to the *Tikhonov* regularization and selects the solution with the smallest L₂-norm. The second one ensures a smooth evolution by penalizing unphysical jumps between consecutive time steps. While we set $\lambda = 0.9$, the model is robust to variations in this hyperparameter.

Parameter Determination

The parameters used for the model combine physical constraints from literature with data-driven optimization. The rate constants in our model follow the Arrhenius equation, $K_i = Ae^{-E_i/RT}$, which depends on:

- Energy Barriers or Adsorption Enthalpies (E_i)
- Steric Factors (A_i)

The Energy Barriers for the fast and slow chemical reactions from the reaction scheme were adopted directly from [1].

The Steric Factors of the fast and slow reactions were determined through a data-driven optimization. Those parameters were fitted by minimizing the error between our model's predictions and the experimental dataset from [1].

Results

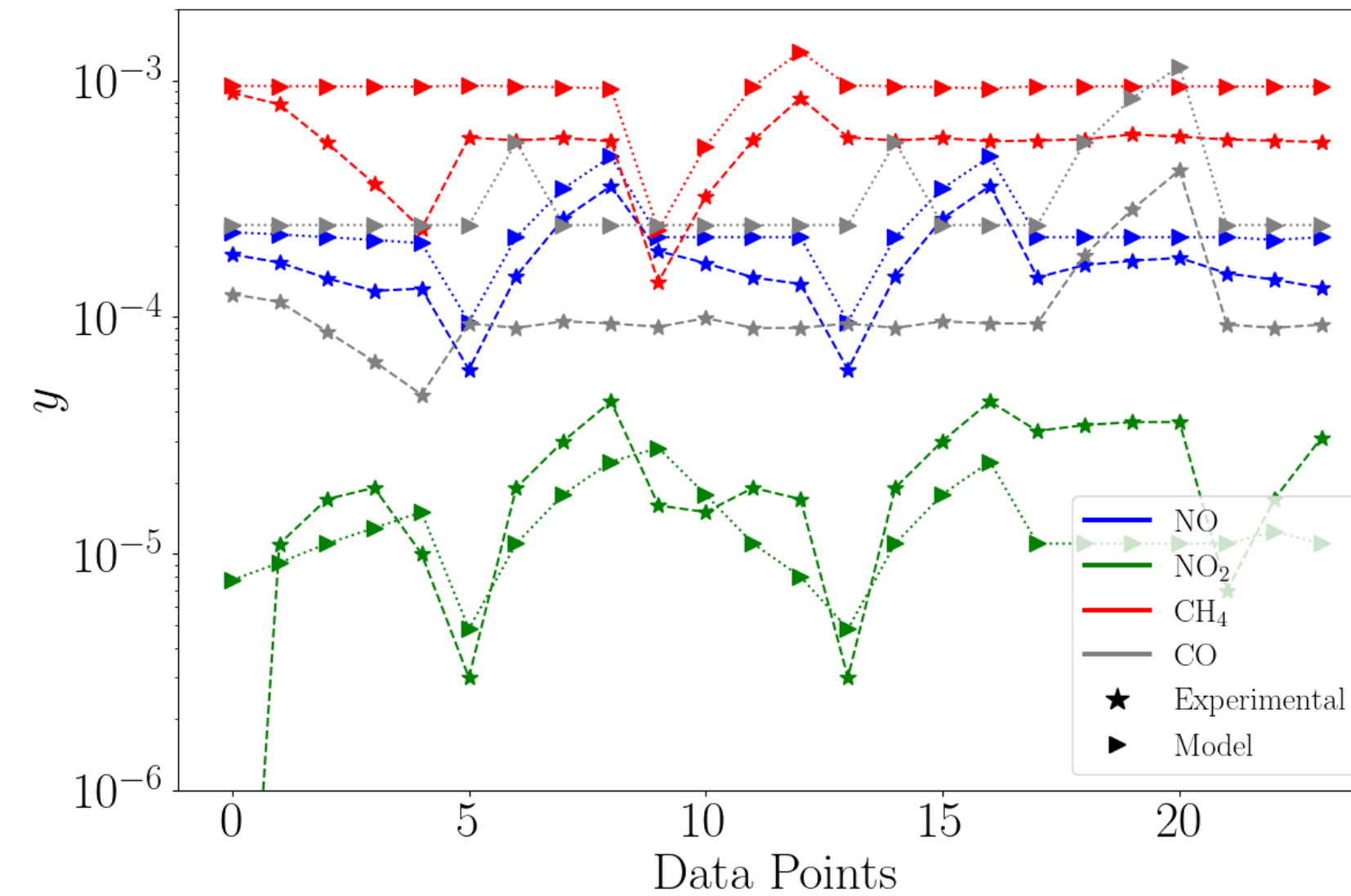
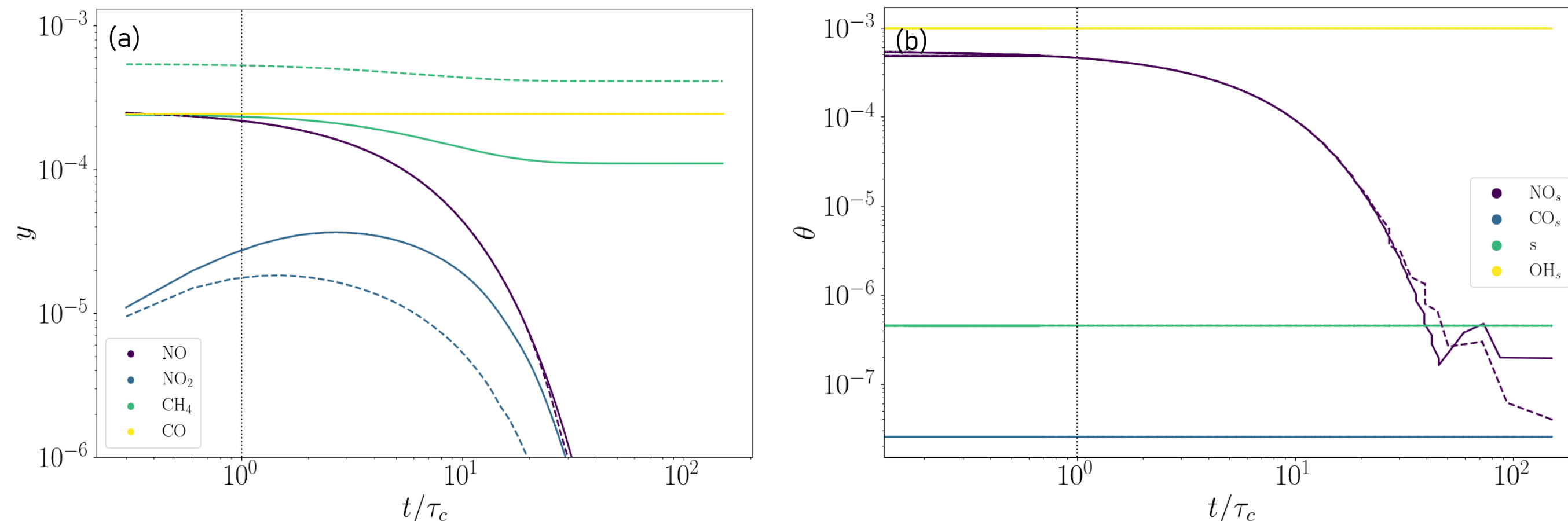


Figure 1: Comparison of DAE model predictions against experimental data [1] of fractions of key species (NO, NO₂, CH₄ and CO). Experimental conditions: 429–520°C, with fixed H₂O (13%), O₂ (6.8%) and CO₂ (7.8%). Inlet concentrations of CO, NO, and CH₄ vary for each point, but their sum is around 1500 ppm.

As shown in Figure 1, our DAE model reproduces the experimental trends observed by [1], The model captures the behavior of NO_x species across a range of operating temperatures and inlet concentrations. However, the model consistently overpredicts CH₄ and CO fractions.



Figures 2: Simulated temporal evolution of key chemical species fractions under experimental conditions. The conditions were set to 478°C with a gas mixture of H₂O (13%), O₂ (6.8%), CO₂ (7.8%), CO (245 ppm) and NO (260 ppm). (a) Normalized density (γ) of key gas-phase species. (b) Surface coverage (θ) on the catalyst's sites s . Simulations were performed with two different CH₄ concentrations: 240 ppm (solid lines) and 540 ppm (dashed lines).

As shown in Figure 2, CH₄ and NO are consumed over time. Moreover, NO₂ is formed and subsequently destroyed.

The results from Figure 1 were obtained with residence time $t = \tau_c \approx 0.04$ secs, replicating the experimental conditions.

Conclusions:

- The model captures the qualitative trends and temporal evolution of the key reactive gaseous species (NO, NO₂, CH₄ and CO), but it consistently underpredicts the final concentrations of CO and CH₄ when compared to experimental data.
- The disagreement suggests that the model's core assumptions for surface evolution are too restrictive. Relaxing these assumptions is the primary path towards improving quantitative accuracy.
- The model predicts that the residence time required for significant CH₄ removal is ~ 20 times the catalytic residence time (τ_c) from [1], providing a clear hypothesis for future experimental validation.

Perspectives:

- Extend the model to simulate industrially relevant conditions, such as bairn air treatment, which involves higher CH₄ concentrations (up to 1%) and the effects of plasma activation (NO_x up to 5%).
- Enhance the model's predictive power by replacing empirical parameters with high-fidelity energy barriers computed from first-principle simulations (DFT and Molecular Dynamics).

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Acknowledgements:

This work was supported by FCT (Fundação para a Ciência e a Tecnologia), under funding to IPFN: UIDB/50010/2020 (<https://doi.org/10.54499/UIDB/50010/2020>), UIDP/50010/2020 (<https://doi.org/10.54499/UIDP/50010/2020>), LA/P/0061/2020 (<https://doi.org/109.54499/LA/P/0061/2020>); and by European Union under Horizon Europe project CANMILK (DOI:10.3030/101069491).