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**Microkinetic Modeling on Nascent Decomposition
Pathways of CH₄ Pyrolysis In Gas-Phase ZnCl₂
Catalyst**

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Nascent decomposition pathways of CH₄ in gas-phase

ZnCl₂

- **Abstract** : Methane pyrolysis is one of the methods to produce hydrogen on large scale in industries. Methane, upon decomposition, gives Hydrogen which is then used for multiple purposes including energy applications. Microkinetic modeling study to understand the nascent decomposition pathways of methane pyrolysis, catalyzed by gas-phase ZnCl₂, in a constant pressure batch reactor at 1273 K. We find that ZnCl₂ catalyzes methane pyrolysis with an apparent activation energy of 227 kJ/mol. We have also performed sensitivity analysis on a reaction network comprising initiation, termination, and primary propagation reactions.
- **Introduction**: Steam reforming of hydrocarbons is the main industrial process for manufacturing hydrogen.¹ The process generates large quantities of CO₂ as a side-product. Methane pyrolysis is a possible alternative for producing hydrogen without generating CO₂. The rate of methane pyrolysis in gas phase is low; it is also difficult to carry out because the carbon produced by the reaction clogs the equipment. Ordinary heterogeneous catalysts cannot be used because they are rapidly deactivated by coking. It is however possible to perform the reaction by using a molten catalyst in a bubble column. The molten catalyst could be a metal, or a metallic alloy, or a mixture of molten salts.
- **Methodology: The Computation of Rate Coefficient** : Methane pyrolysis by gas-phase ZnCl₂ is a combination of unimolecular and bimolecular reactions (vide infra). We obtained the microscopic rate coefficients using transition-state theory (TST). The TST rate coefficient (k^{TST}) is estimated using.

$$k_{TST} = \sqrt{\frac{k_B T}{2\pi m}} \frac{Q^\ddagger}{Q_R/V^{\nu-1}}$$

where ,

k_B = Boltzmann constant.

m = mass of the system.

Q^\ddagger = partition function of the transition-state.

Q_R = partition function of the reactants.

V is the volume.

Rate Equation

$$r_l = \sum_{j=1}^m r_{lj} = \frac{1}{V} \frac{dN_l}{dt} = - \sum_{j=1}^m k_j \prod_{i=1}^n \left(\frac{N_i}{V} \right)^{\nu_{ij}^l} + \sum_{j=1}^m k_{-j} \prod_{i=1}^n \left(\frac{N_i}{V} \right)^{\nu_{ij}^l}$$

Where,

V = Volume of the reaction mixture

N_i = Moles of species i

k_j = Forward reaction rate constant

k_{-j} = Backward reaction rate constant

ν_{ij} = Stoichiometric coefficient

- **Sensitivity Analysis using Degree of Reaction Control:** Sensitivity Analysis. Methane pyrolysis involves a complex network of several elementary reactions. For such complex reaction network, the information about the rate-determining steps becomes nontrivial and cannot be obtained just from the reaction mechanisms and rate coefficients. There may be more than one step controlling the overall performance therefore, obtained the information on the critical reaction steps by performing sensitivity analysis using the concept of degree of rate control (DRC). DRC predicts the changes in the overall rate of consumption up on small changes in one of the kinetic parameters.

$$X_i = \frac{k_i}{r} \left(\frac{\partial r}{\partial k_i} \right)_{k_{j \neq i}, K_j} = \left(\frac{\partial [\ln r]}{\partial [\ln k_i]} \right)_{k_{j \neq i}, K_j}$$

Where,

K_i = Equilibrium constant for ith reaction.

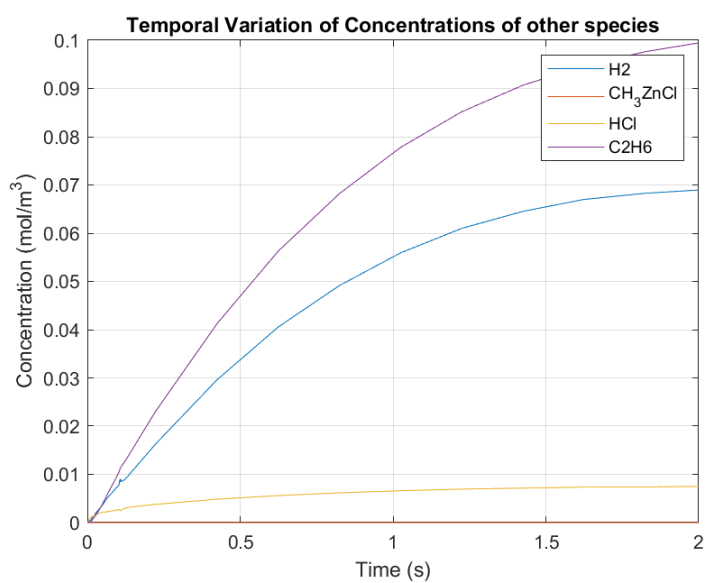
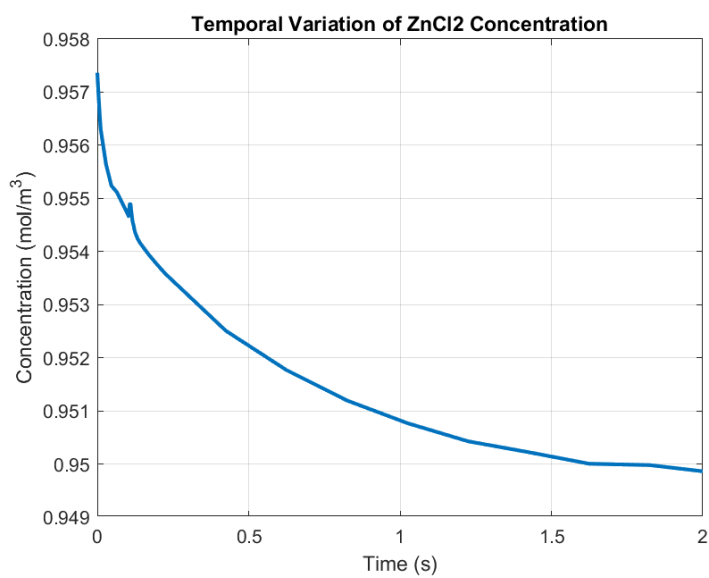
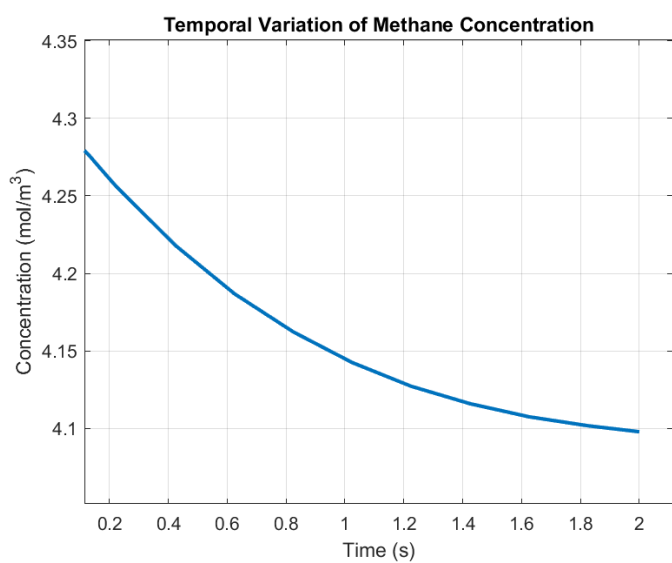
r = Rate of reaction.

X_i = DRC Parameter.

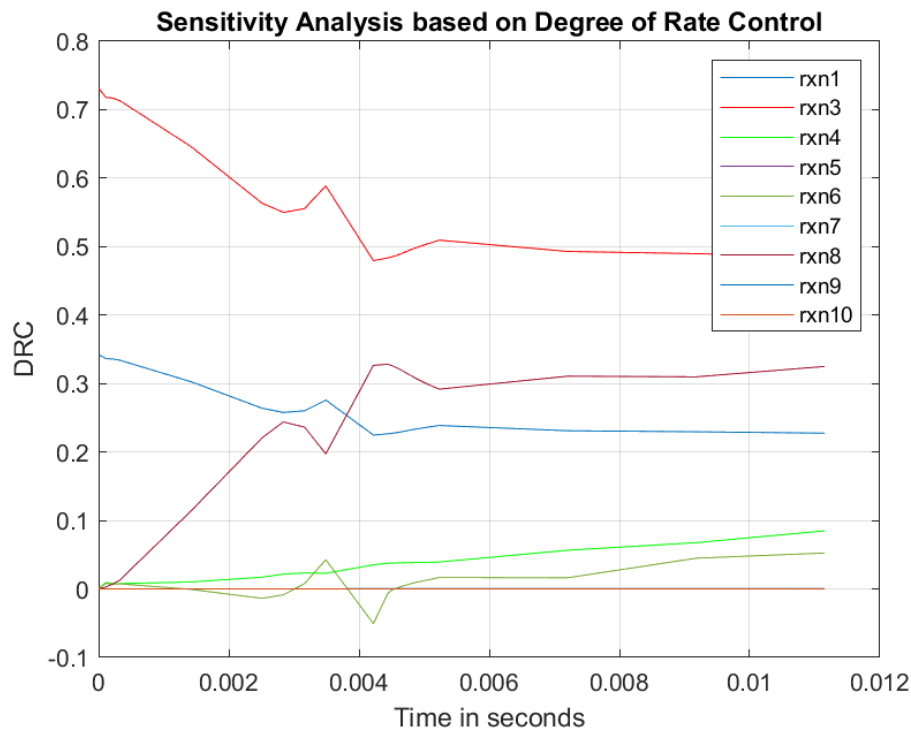
k_i = Rate constant for ith reaction.

Now, if the value of X_i is non zero for a reaction then that reaction may be rate limiting and if X_i value is zero for a reaction then that reaction will not be rate limiting.

➤ **Plots of Concentration v/s Time:**



➤ **Degree of Rate Control (xi) v/s Time:**



➤ **Results and Conclusions:**

- Methane Concentration initially decreases rapidly and then slowly, which fitted to $A \exp(-k_{A1}t) + B \exp(-k_{A2}t)$. ZnCl_2 concentration is also decreases w.r.t time and the product concentration is increases w.r.t time.
- Sensitivity analysis based on degree of rate control (DRC) to gauge the rate controlling steps. As we can see simulations suggests that the initial reaction network can be simplified to four reactions, which will be rate controlling, reaction 3,4,8,and 9 which has a significant value of xi (DRC). Reaction 10 is not that significant and almost tending to zero.
- Therefore reaction 3,4,8 and 9 are the rate limiting reactions.