A Review Paper

On

Microkinetic Modeling of Methane Pyrolysis over Gas-Phase Na Catalyst

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1 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. Here, pyrolysis of methane is carried out at 1 atm pressure, in the presence of Na (Sodium) catalyst at 973 K temperature. Partial pressure of methane and argon gases is 0.45 atm, while for sodium it is 0.45 atm. Based upon the reaction kinetics and mechanisms, a data of concentration of CH_4 vs time is calculated and plotted. Also, the sensitivity analysis of all the reaction schemes involved in methane pyrolysis is carried out using Degree of Reaction Control (DRC) and plotted as a function of time to find out the rate-limiting reaction steps.

2 INTRODUCTION

Steam reforming of hydrocarbons is the primary industrial method for hydrogen production but results in significant CO_2 emissions. Methane pyrolysis offers a CO_2-free alternative, but it faces challenges, including slow gas-phase reactions and equipment clogging due to carbon formation. However, these issues can be mitigated by using a catalyst. This catalyst can be composed of metals, metallic alloys, or molten salt mixtures. Here, Na metal is used as a heterogeneous catalyst.

3 METHODOLOGY

From experimental studies, multiple reaction steps are devised. Here, a total of 24 reaction steps are devised out of which some are unimolecular and other are bimolecular.
Now the rate coefficients for all 24 reactions are calculated based upon the transition state theory, which is stated as:

$$\mathrm{k}_{tst} = \left(\sqrt{\frac{K_b T}{2\pi m}}\right) * \left(\frac{Q^{\#}}{\frac{Q^r}{V^{\nu-1}}}\right)$$

Where,
k_{tst} = Rate constant
K_b = Boltzmann constant
m = Mass of the system
V = Volume
ν = 1 for unimolecular reaction and 2 for by molecular reaction.

3.1 Rate Equation

$$Rate = \frac{1}{V}\frac{dN}{dt} = -\sum_{j=1}^{m} k_j \prod_{i=1}^{n} \left(\frac{N_i}{V}\right)^{|\nu_{ij}|} + \sum_{j=1}^{m} k_{-j} \prod_{i=1}^{n} \left(\frac{N_i}{V}\right)^{|\nu_{ij}|} \tag{1}$$

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

3.2 Sensitivity Analysis using Degree of Reaction Control

Now, Sensitivity analysis for methane pyrolysis reaction is done in order to determine which reaction is actually rate limiting. This helps in reducing the computational load by providing the estimate of the equations which actually have impact on the reaction rate.
A method of sensitivity analysis, called Degree of Reaction Control (DRC) is used here to determine the rate-limiting steps from the cluster of reaction steps.
Following is the equation to calculate DRC:

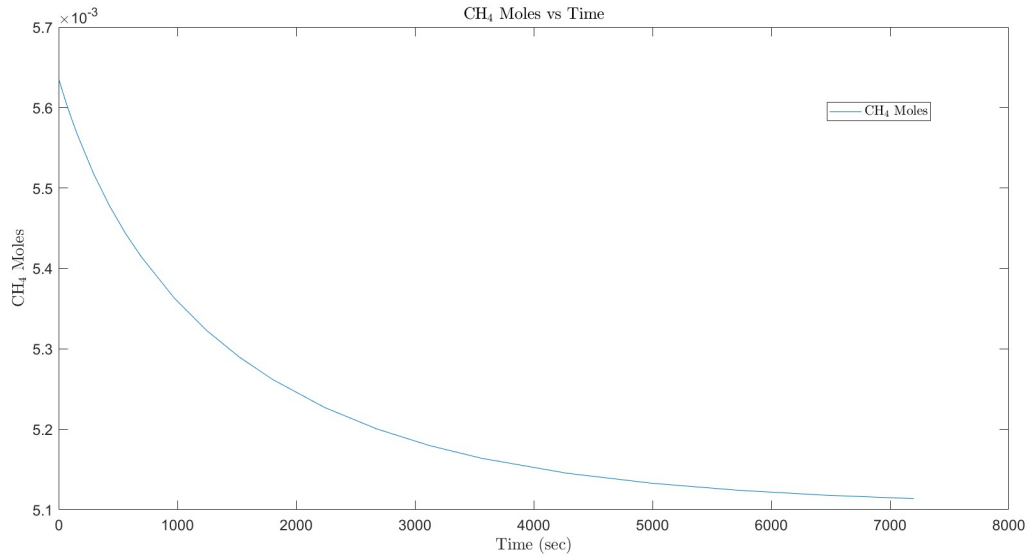
$$X_i = \left(\frac{k_i}{r} * \frac{\partial r}{\partial k_i}\right)_{k_{i\neq j}, K_j} = \left(\frac{\partial [ln(r)]}{\partial [ln(k_i)]}\right)_{k_{i\neq j}, K_j} \tag{2}$$

Where,
K_i = Equilibrium constant for i^{th} reaction
r = Rate of reaction
X_i = DRC Parameter
k_i = Rate constant for i^{th} 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.

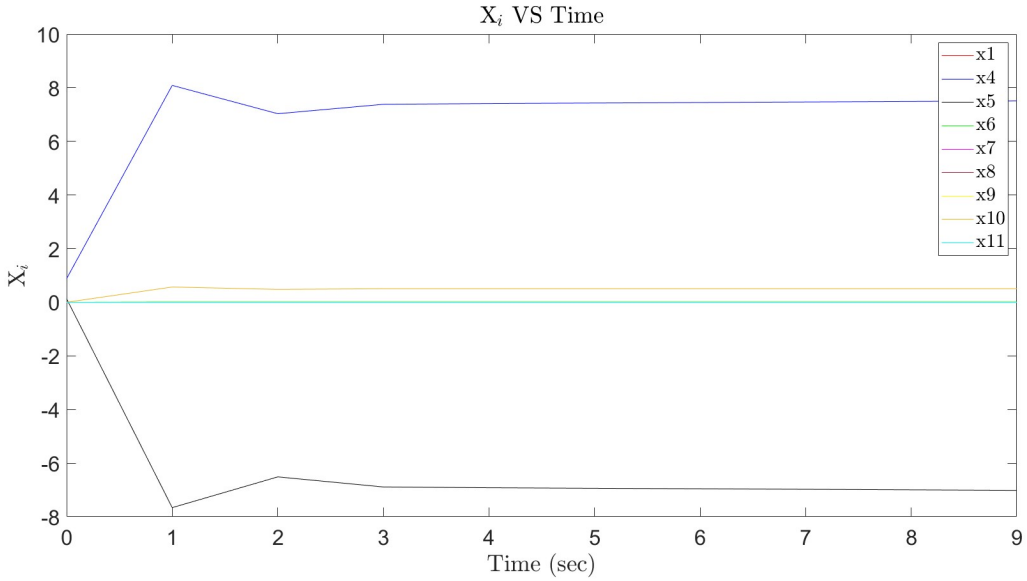
3.3 Result Plots

3.3.1 Methane Moles plot



From the above plot, we can see that the concentration of $CH_4$is decreasing with respect to time.

3.3.2 DRC Plot



From the above plot, we can see that X_i is non zero for 3 reactions, Reaction 4, 5 and 9.
Hence reactions 4, 5 and 9 can be called as rate limiting reactions.