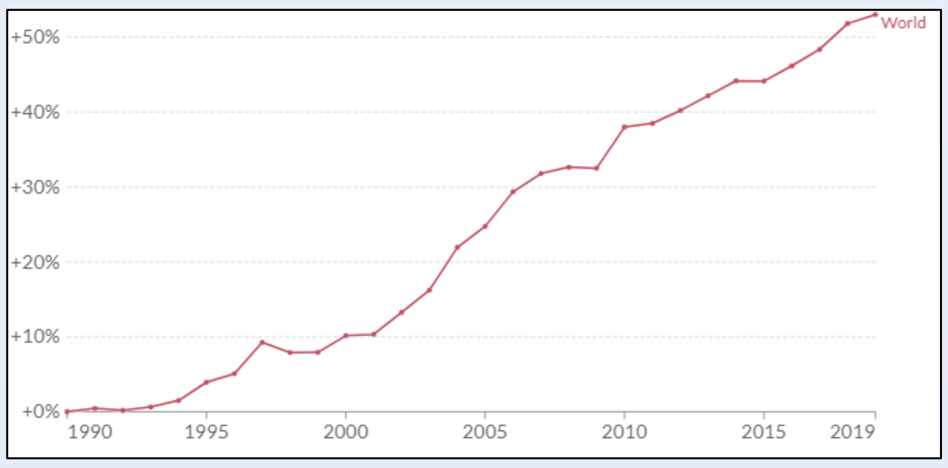
Modelling Methane Pyrolysis in Molten Sodium Catalyst

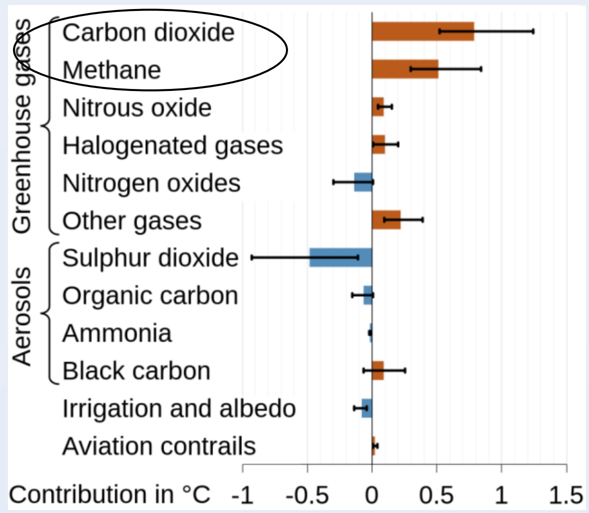
Sunny Kumar Bhagat[1], Nikil Surya R[1], Horia Metiu[3], Vishal Agarwal[1,2*]

[1]Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India
[2]Department of Sustainable Energy Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India
[3]Department of Chemistry and Biochemistry, University of California-Santa Barbara, Santa Barbara, California 93106-9510, United States
*Corresponding author. E-mail: vagarwal@iitk.ac.in

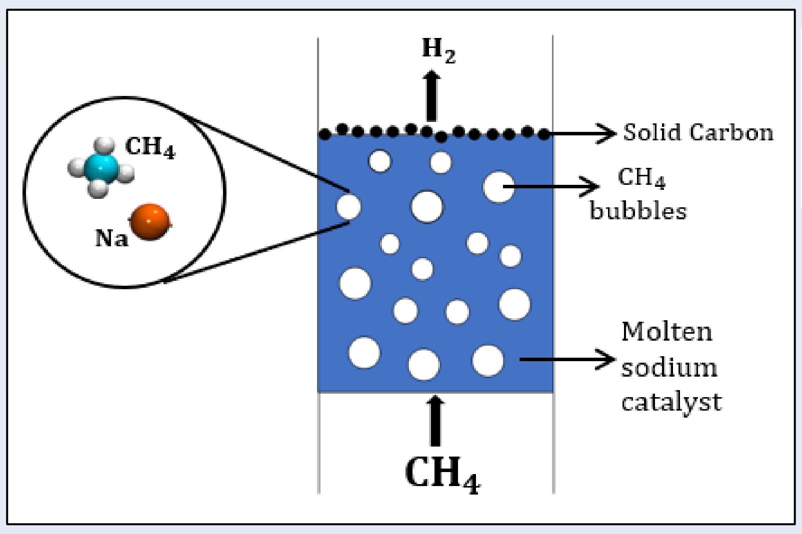
MOTIVATION



Percentage change in total GHGs since 1990



OBJECTIVE



Method 1
Steam Reforming of Methane
$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$

Method 2
Pyrolysis of Methane
$CH_4(g) \rightarrow 2H_2(g) + C(s)$

❖ Can Sodium as a system, acts as an effective catalyst for methane pyrolysis?

RESULTS & DISCUSSIONS

❑ Conversion of Methane by gas-phase Sodium

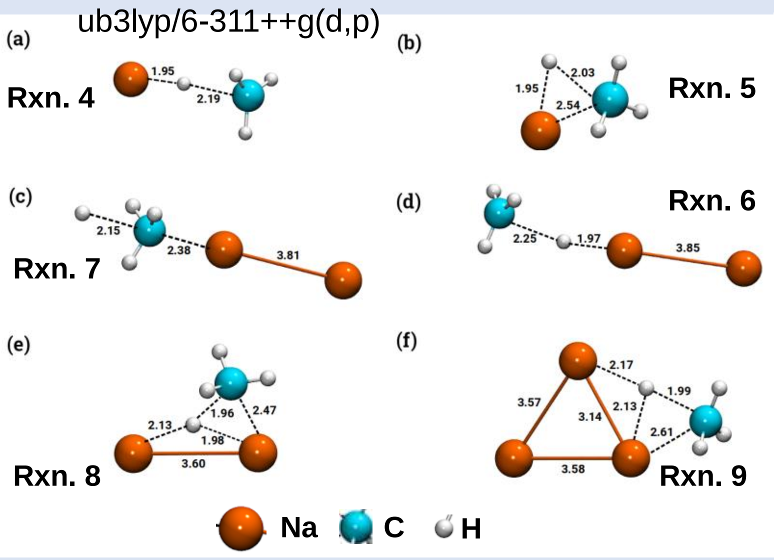
- Reaction Mechanisms, Thermodynamic and Kinetic Parameters*

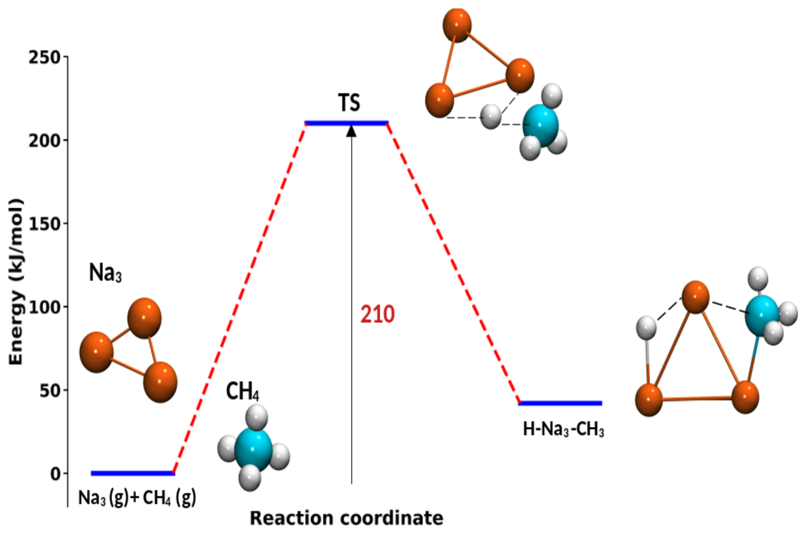
Theory and basis set: ccsd(t)/aug-cc-pvqz or ccsd/6-311++g(d,p)

No.	Reactions (rxn)	$\Delta E_f^\ddagger$	$\Delta H_f^\ddagger$	$T\Delta S_f^\ddagger$	$\Delta G_f^\ddagger$	k_i	$\Delta E_b^\ddagger$	$\Delta H_b^\ddagger$	$T\Delta S_b^\ddagger$	$\Delta G_b^\ddagger$	k_{-i}
Initiation reactions											
1	$CH_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3^* + H^*$	468	443	47	396	1.1(-8)	-	-	-	-	4.1(-10)
2	$Na_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2Na$	69	61	-13	74	2.2(9)	-	-	-	-	1.5(-9)
3	$Na_3 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Na_2 + Na$	28	11	-28	40	1.5(11)	-	-	-	-	4.4(-9)
4	$CH_4 + Na \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} NaH + CH_3^*$	288	267	-14	281	2.2(-21)	6	9	-68	78	1.9(-10)
5	$CH_4 + Na \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} HNaCH_3$	278	257	-39	297	3.2(-22)	12	3	-66	69	4.1(9)
6	$CH_4 + Na_2 \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} Na_2H + CH_3^*$	343	331	6	324	1.0(-23)	54	62	-53	114	1.9(-12)
7	$CH_4 + Na_2 \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} Na_2CH_3 + H^*$	381	366	-15	381	9.4(-27)	-8	-11	-97	86	6.6(-11)
8	$CH_4 + Na_2 \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} HNa_2CH_3$	272	259	-59	318	2.3(-23)	208	200	0.4	200	3.9(2)
9	$CH_4 + Na_3 \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} HNa_3CH_3$	210	202	-76	278	3.1(-21)	168	161	0.3	161	4.7(4)
Primary propagation reactions											
10	$CH_4 + H^* \underset{k_{-10}}{\overset{k_{10}}{\rightleftharpoons}} CH_3^* + H_2$	62	49	-74	123	6.9(-13)	50	44	-117	162	5.7(-15)
11	$CH_4 + CH_3^* \underset{k_{-11}}{\overset{k_{11}}{\rightleftharpoons}} C_2H_6 + H^*$	215	215	-110	325	9.9(-24)	150	415	237	179	6.8(-16)
12	$HNaCH_3 \underset{k_{-12}}{\overset{k_{12}}{\rightleftharpoons}} NaCH_3 + H^*$	15	6	-56	62	9.5(9)	-	-	-	-	3.3(-9)
13	$HNaCH_3 \underset{k_{-13}}{\overset{k_{13}}{\rightleftharpoons}} NaH + CH_3^*$	15	7	-37	44	8.7(10)	-	-	-	-	7.3(-9)
14	$NaH \underset{k_{-14}}{\overset{k_{14}}{\rightleftharpoons}} Na + H^*$	187	177	1	177	6.8(3)	-	-	-	-	3.0(-9)
15	$NaCH_3 \underset{k_{-15}}{\overset{k_{15}}{\rightleftharpoons}} Na + CH_3^*$	139	44	-93	138	8.4(5)	-	-	-	-	2.3(-10)
16	$Na_2H \underset{k_{-16}}{\overset{k_{16}}{\rightleftharpoons}} Na_2 + H^*$	180	170	-6	176	7.1(3)	-	-	-	-	1.4(-9)
17	$Na_2H \underset{k_{-17}}{\overset{k_{17}}{\rightleftharpoons}} Na + NaH$	62	54	-14	67	5.0(9)	-	-	-	-	1.5(-9)
18	$Na_2CH_3 \underset{k_{-18}}{\overset{k_{18}}{\rightleftharpoons}} Na_2 + CH_3$	80	73	-12	85	5.8(8)	-	-	-	-	3.1(-9)
19	$Na_2CH_3 \underset{k_{-19}}{\overset{k_{19}}{\rightleftharpoons}} Na + NaCH_3^*$	224	216	-38	254	4.4(-1)	-	-	-	-	3.7(-12)
20	$Na_3H \underset{k_{-20}}{\overset{k_{20}}{\rightleftharpoons}} Na_2 + NaH$	102	93	-4	97	1.4(8)	-	-	-		5.1(-10)
21	$Na_3H \underset{k_{-21}}{\overset{k_{21}}{\rightleftharpoons}} Na_3 + H^*$	261	251	29	222	2.4(1)	-	-	-	-	5.0(-10)
22	$Na_3H \underset{k_{-22}}{\overset{k_{22}}{\rightleftharpoons}} Na_2H + Na$	109	94	-30	124	4.7(6)	-	-	-	-	3.9(-11)
Termination reactions											
23	$H^* + H^* \underset{k_{-23}}{\overset{k_{23}}{\rightleftharpoons}} H_2$	-	-	-	-	1.9(-10)	457	430	1	430	1.8(-10)
24	$CH_3^* + CH_3^* \underset{k_{-24}}{\overset{k_{24}}{\rightleftharpoons}} C_2H_6$	-	-	-	-	2.8(-10)	404	387	72	315	2.7(-4)

- Transition States of selected reactions involving Sodium Clusters as reactants

ub3lyp/6-311++g(d,p)





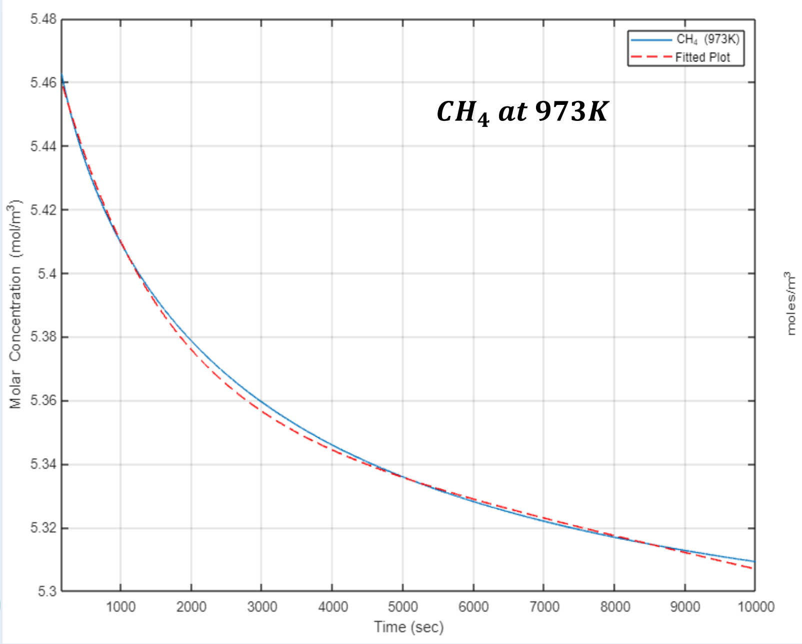
- Microkinetic Model and Simulations

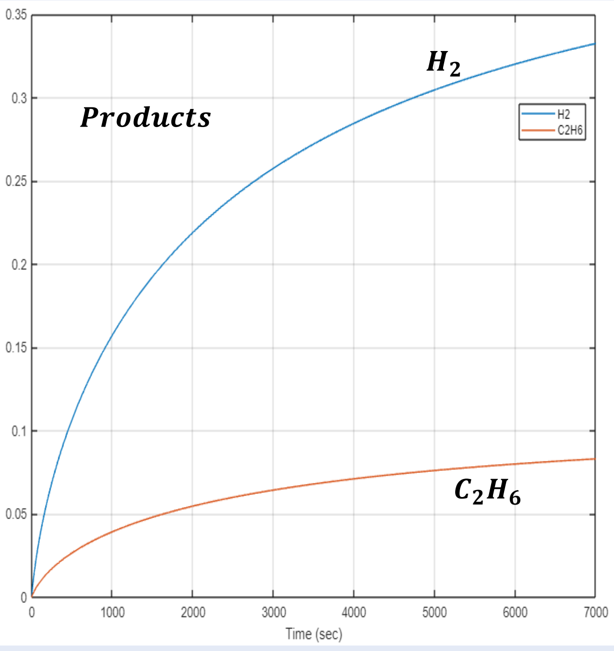
General Rate Expression (Solved using **ODE15s** in MATLAB):

$$r_l = \sum_{j=1}^{m} r_{lj} = \frac{1}{V}\frac{dN_l}{dt} = -\sum_{j=1}^{m} k_j|v_{ij}| \prod_{\substack{i=1\\(v_{ij}<0)}}^{n} \left(\frac{N_i}{V}\right)^{|v_{ij}|} + \sum_{j=1}^{m} k_{-j}|v_{ij}| \prod_{\substack{i=1\\(v_{ij}>0)}}^{n} \left(\frac{N_i}{V}\right)^{|v_{ij}|}$$

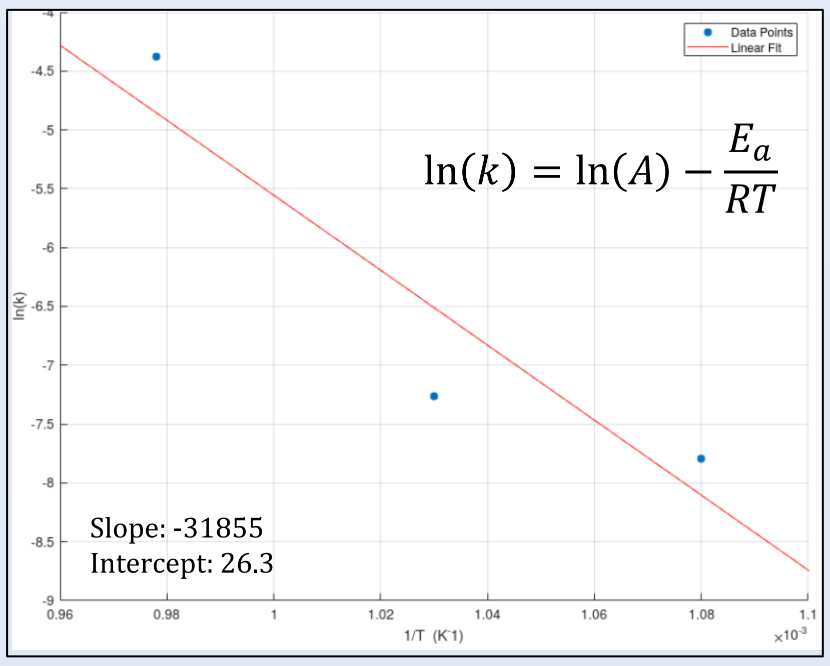
where; $k_{TST,uni} = e.\frac{k_BT}{h} e^{\frac{\Delta S}{R}} e^{\frac{-E_a}{RT}}$ & $k_{TST,bi} = \frac{k_BT}{h}\frac{k_BT}{P} e^{\frac{\Delta S}{R}} e^{\frac{-E_a}{RT}}$ | Volume = $1m^3$

ICs: $P_{CH_4} \& P_{Ar} = 0.44\ atm\ each$; $P_{Na} = 0.076\ atm$; $P_{Na_2} = 0.023\ atm$; $P_{Na_3} = 0.001\ atm$





- Apparent Activation Energy

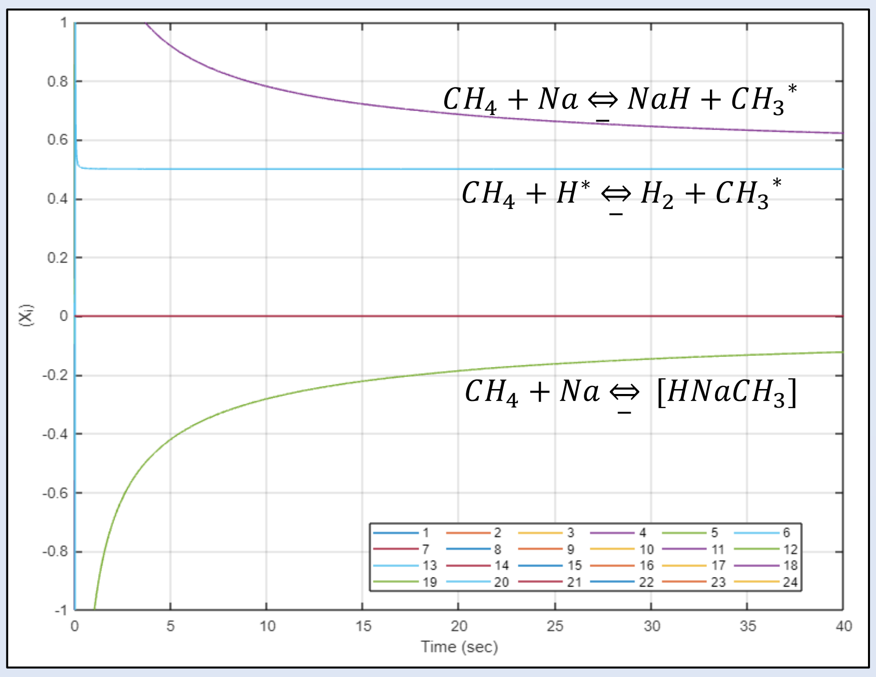


Temperature, K	k values (s^{-1})
923	**4.1*10^{-4}**
973	**7.1*10^{-4}**
1023	**1.3*10^{-2}**

Results

Parameters	Values
A	$2.6*10^{11}\ s^{-1}$
E_a	265 kJ/mol
$E_{a,w/o\ catalyst}$	423 kJ/mol

- Sensitivity Analysis by Degree of Rate Control (DRC)

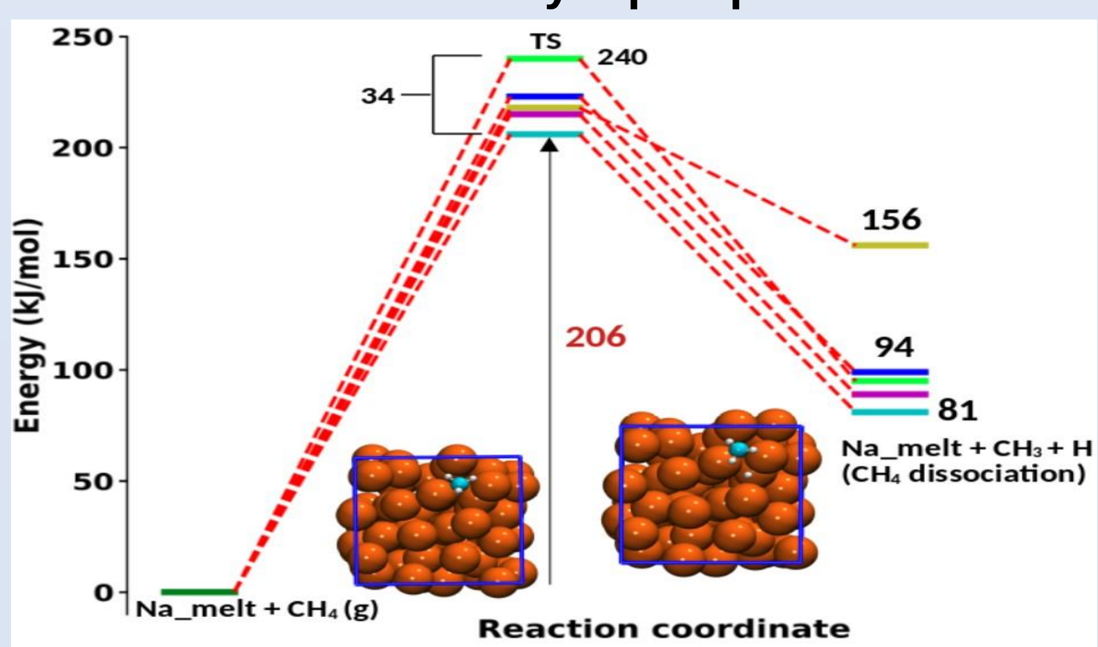


$$X_i = \left(\frac{\partial \ln(r)}{\partial \ln(k_i)}\right)_{k_{j\neq i};K_j}$$

$$Constraint: \sum_{i=1}^{n} X_i = 1$$

Note: In simulations, both forward as well as backward rate constants were altered by 10%

❑ Conversion of Methane by liquid-phase Sodium



❑ Conclusion

- Na$_3$ was found to be the most active cluster amongst all sodium clusters, with forward electronic energy barrier of 210 kJ/mol.
- Calculations for methane pyrolysis in gas-phase are highly accurate, resulting the apparent E_a as 265 kJ/mol whereas that in liquid-phase with E_a ranging between 206 – 240 kJ/mol.
- Sensitivity analysis based on DRC suggests that three elementary reactions as RDS, amongst which the most dominant are $CH_4 + Na \Leftrightarrow NaH + CH_3^*$ and $CH_4 + Na \Leftrightarrow [HNaCH_3]$
- Sodium catalyzes methane pyrolysis and is more active in liquid-phase than that in gas.

Acknowledgement: Ramanujan Fellowship, SERB, Dept. of Science & Technology

❑ References:

(1) https://data.worldbank.org/indicator/EN.ATM.GHGT.KT.CE
(2) “Nascent Decomposition Pathways of CH4 Pyrolysis in Gas-Phase Metal Halides” SK Dutta, S Ghosh, H Metiu, V Agarwal - The Journal of Physical Chemistry A, 2022