Supporting Information

Effect of Synergy on Selective Low-Temperature Dehydrogenation of Propane to Propylene over Defect-Induced Copper Titanium Catalyst

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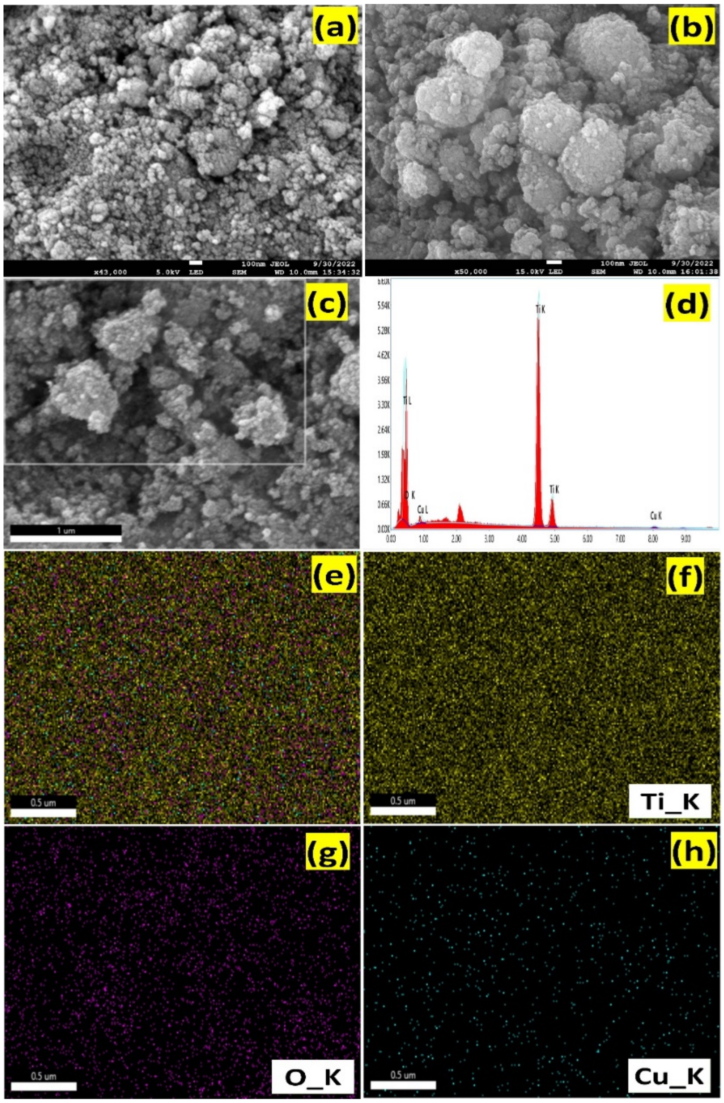


Figure.S1 SEM images of (a-c) Fresh Cu-TiO_2 (d-e) and its corresponding EDS image and mapping of (f)Ti, (g) O, and (h) Cu for fresh Cu-TiO_2 catalyst

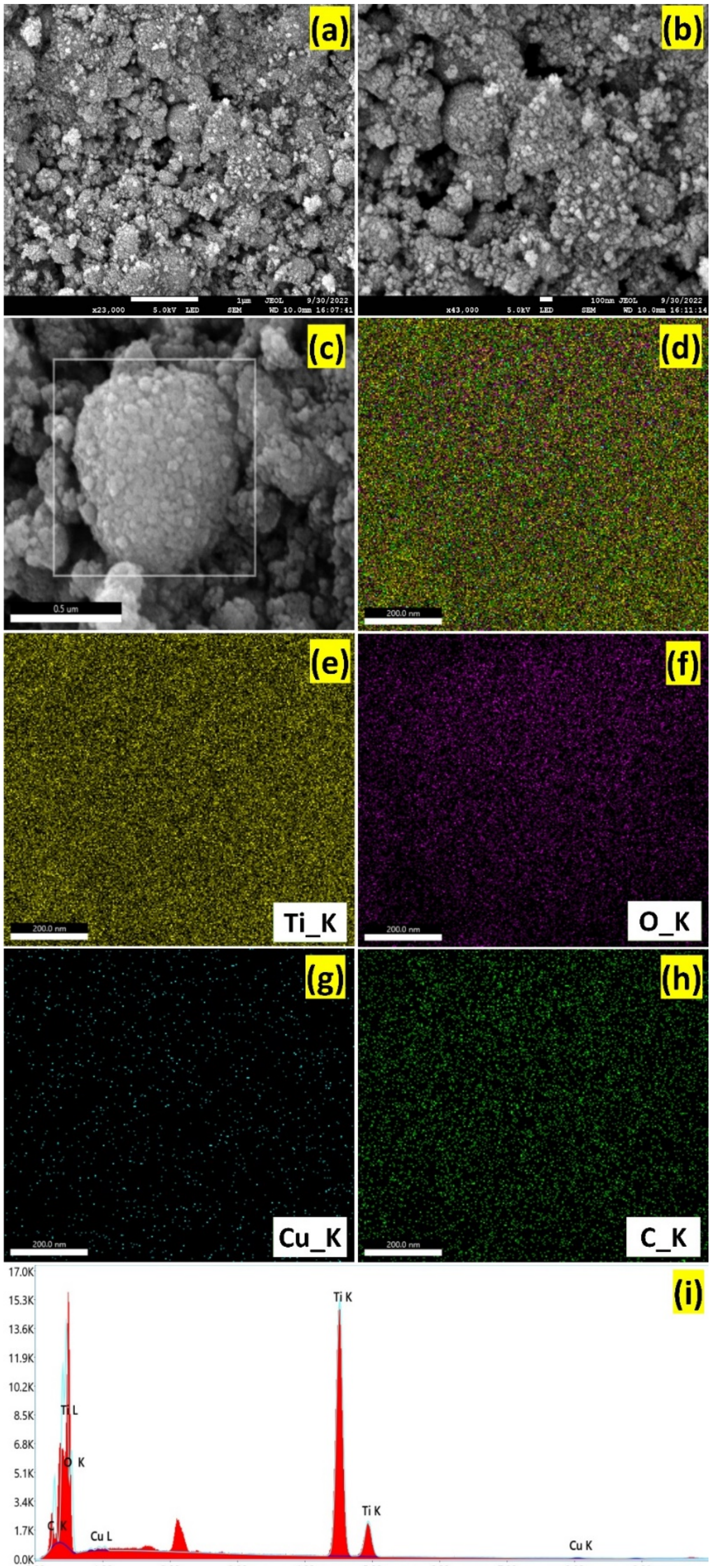


Figure.S2 SEM images of (a-c) spent Cu-TiO_2 (d) Elemental mapping of (e)Ti, (f) O, (g) Cu, (h) C, and (i) its corresponding EDS image for spent Cu-TiO_2 catalyst

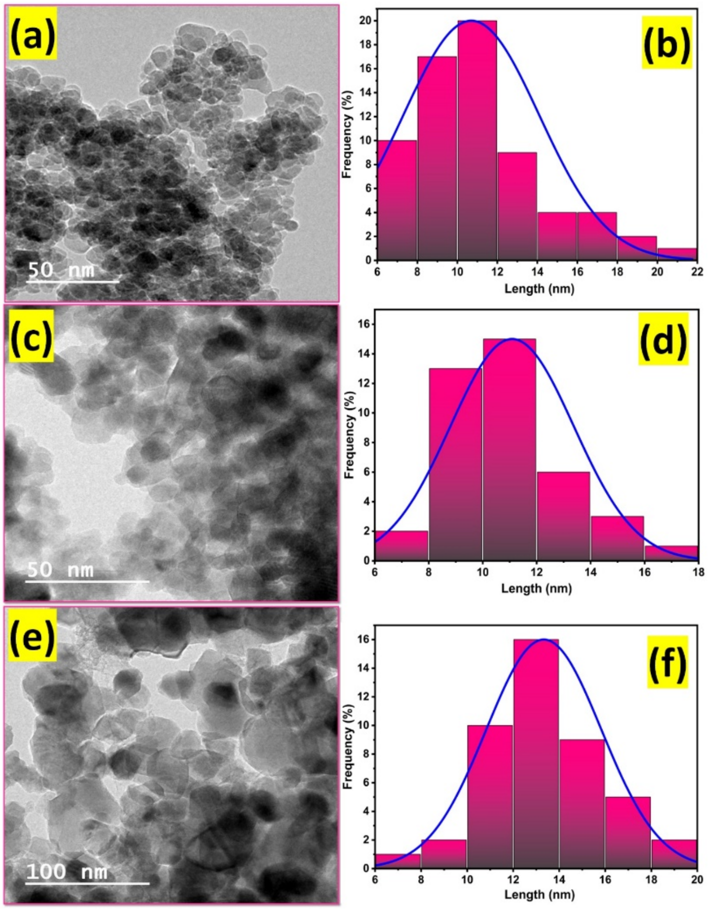


Figure.S3 HRTEM analysis at 50 nm,50 nm and 100 nm resolution of the finely dispersed nanoparticles and their size distribution in the fresh (a-b) TiO_2 (c-d) fresh and (e-f) spent Cu-TiO_2 catalyst, respectively.

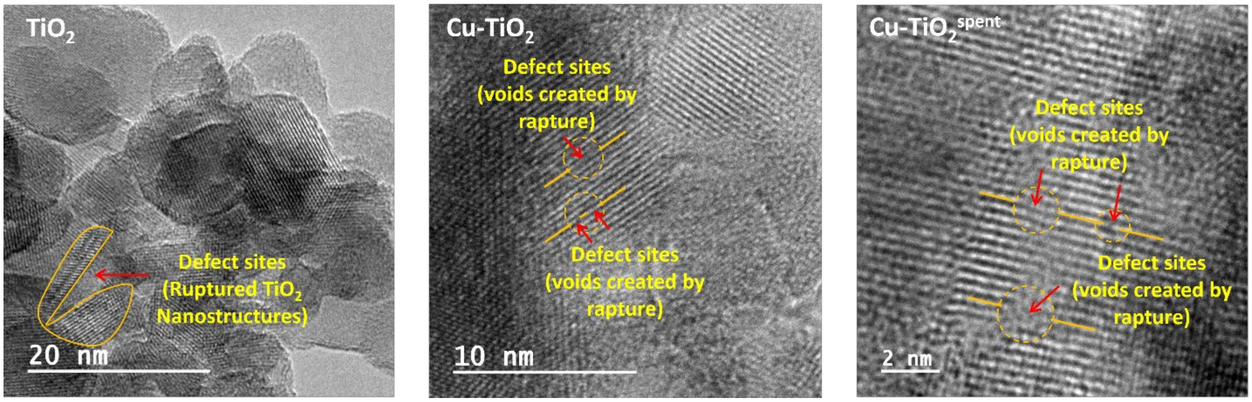


Figure. S4 HRTEM analysis of TiO_2 and fresh & spent Cu-TiO_2 catalyst, indicating defective sites and voids in lattice fringes that resulted in defects.

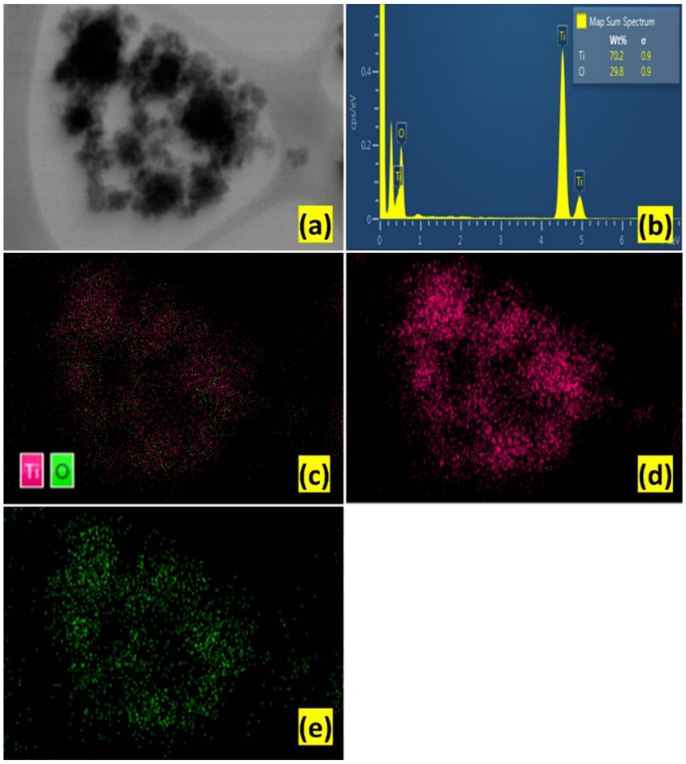


Figure S5. (a) HRTEM image (b) and its corresponding EDS image and (c) elemental mapping of (d) Ti, and (e) O for fresh TiO_2 catalyst

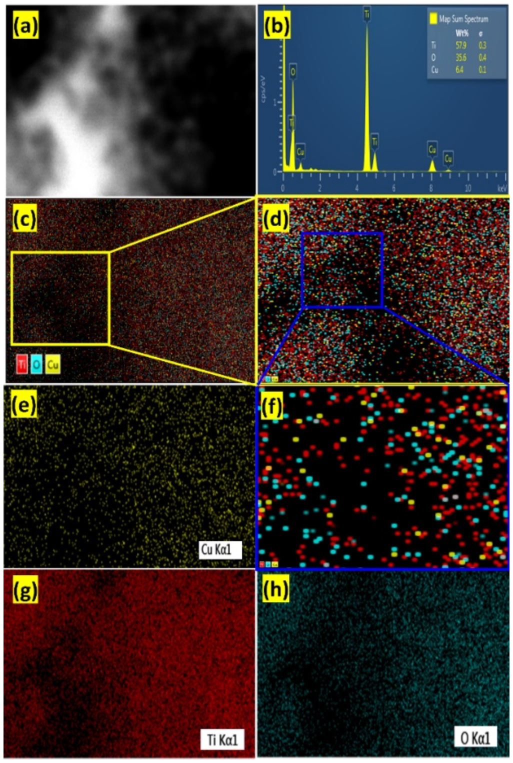


Figure S6. (a) HRTEM image (b) and its corresponding EDS image and (c-d & f) elemental mapping of (e) Cu, (g) Ti, and (h) O for fresh Cu-TiO_2 catalyst

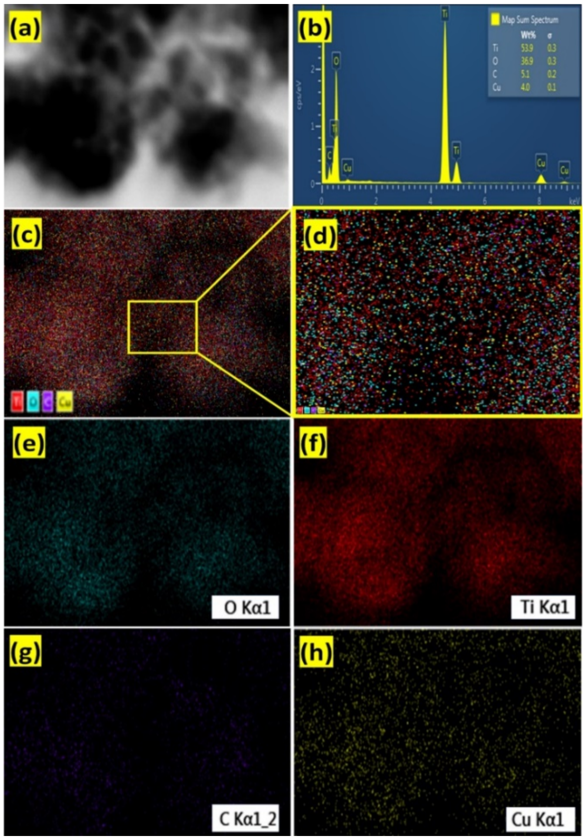


Figure S7. (a) HRTEM image (b) and its corresponding EDS image and (c-d) elemental mapping of (e) O, (f) Ti, (g) C, and (h) Cu for spent Cu-TiO_2 catalyst

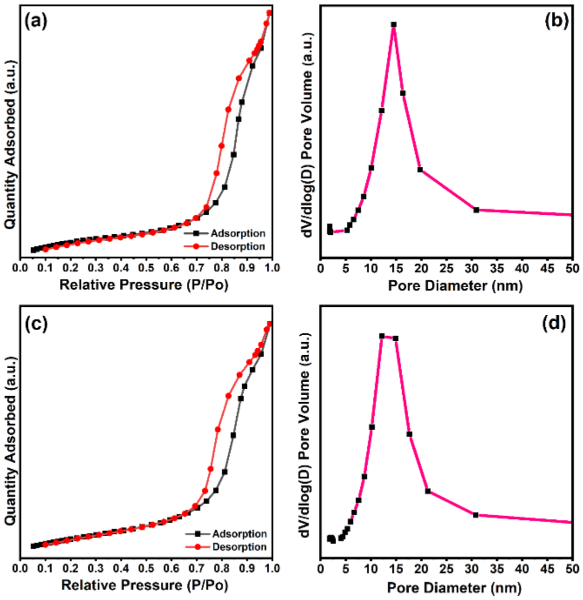


Figure S8. N_2 adsorption-desorption isotherm with Pore size distribution of (a) fresh and (b) spent Cu-TiO_2 catalysts.

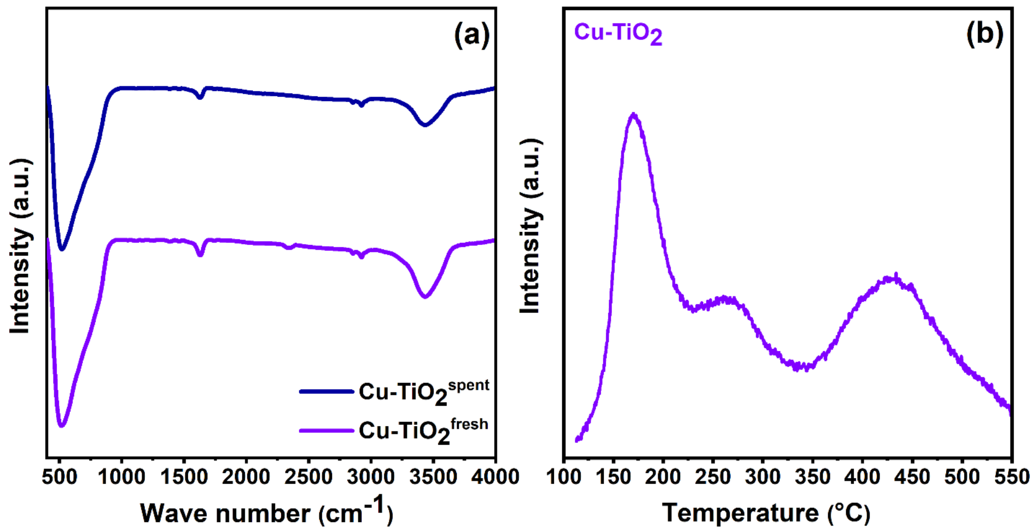


Figure S9. (a) FTIR spectra for fresh and spent [Cu-TiO_2] catalysts, (b) H_2-TPR spectra for fresh [Cu-TiO_2] catalysts.

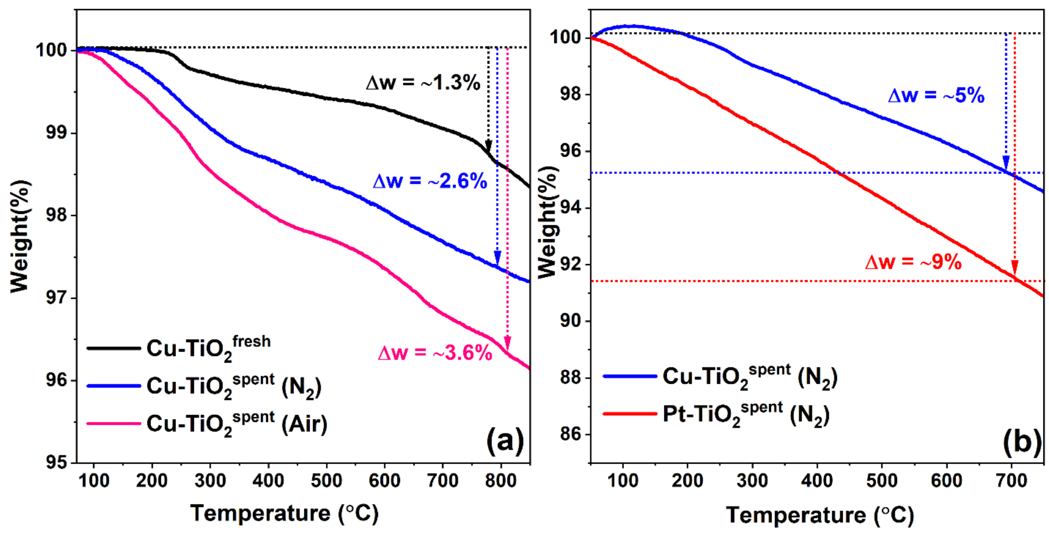


Figure S10. Thermogravimetric analysis profile of (a) fresh and spent Cu-TiO_2 catalyst was recovered after 5h time-on-stream (b) TGA profile of Cu-TiO_2 and Pt-TiO_2 Spent catalyst was recovered after 24h time-on-stream.

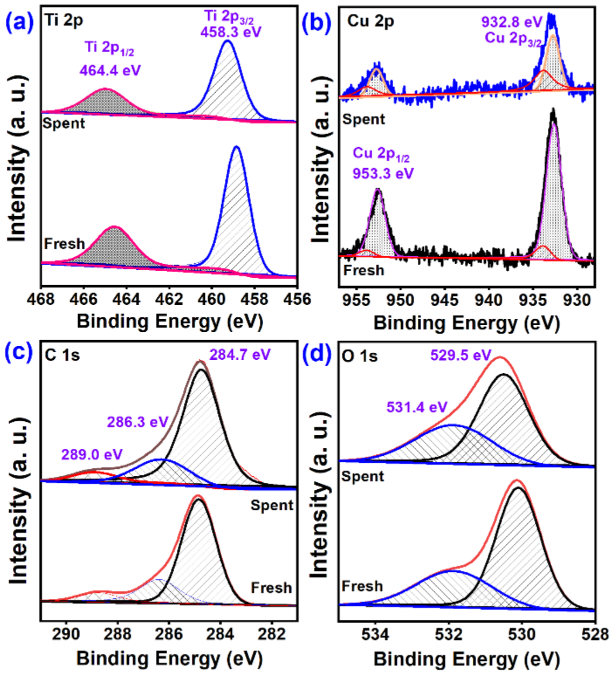


Figure S11. XPS high-resolution scans of (a) Ti 2p, (b) Cu 2p, (c) C 1s and, (d) O1s electrons of fresh (down) and spent(up) [Cu-TiO_2] catalysts.

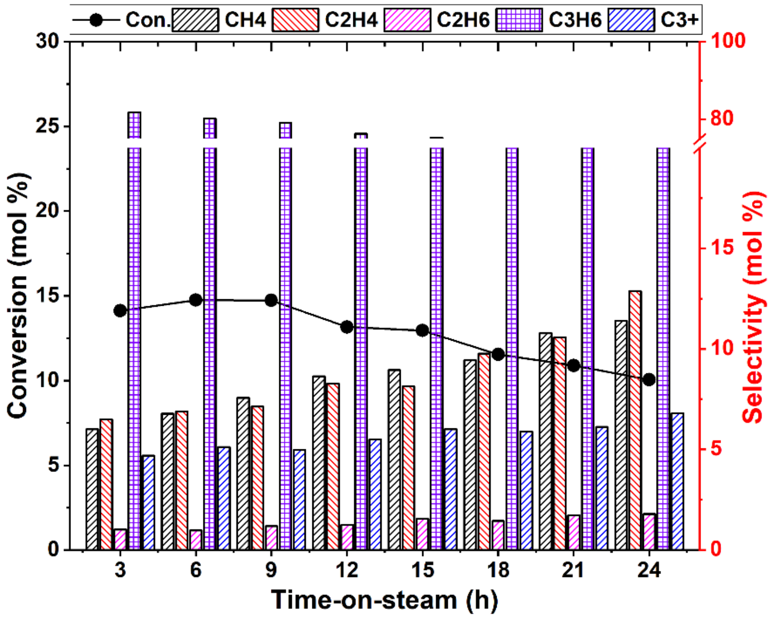


Figure S12. TOS data of the [Pt-TiO_2] catalyst for C_3H_8 conversion and selectivity of C_3H_6. Reaction conditions: Wt. of catalyst-0.25 g (pelletized); reaction temperature, 375 °C; GHSV-4000 h^{-1}

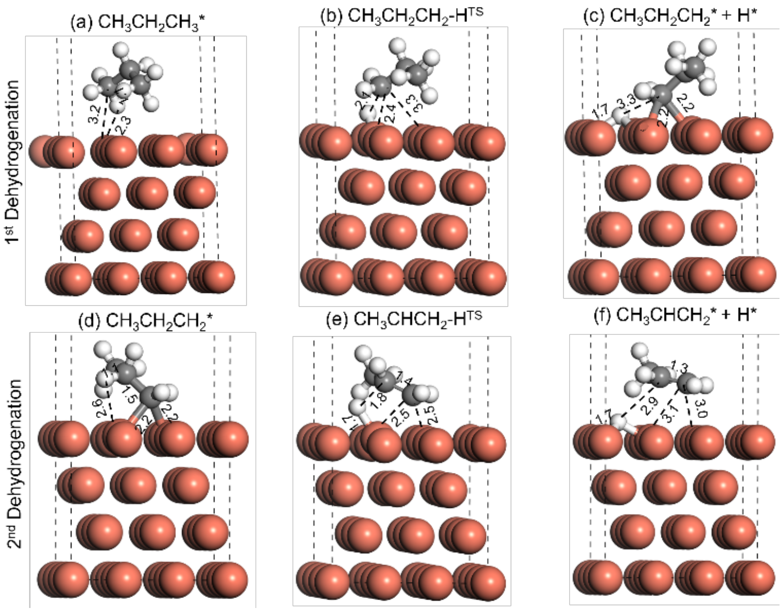


Figure S13. DFT optimized geometry for adsorbates and TS during the propane dehydrogenation to propylene, showing the (a – c) 1st dehydrogenation and (d -f) 2nd dehydrogenation.

Table S1 Summary of performance of different catalysts for dehydrogenation of Propane to Propylene.

Sl. No	Catalyst	Propane Conv. (%)	Selectivity (%)					Propylene Yield	Total Olefin Yield	Production Rate of Propylene ($x10^{-7}$ mmol.g^{-1}.min^{-1})
			CH_4	C_2H_6	C_2H_4	C_3H_6	C_{3+}			
1	Pt/Al_2O_3	4.07	3.52	0.34	5.59	88.94	1.61	3.62	3.91	7.93
2	$Pt\text{-}Sn/Al_2O_3$	1.57	2.19	0.1	4.34	89.81	3.56	1.41	1.53	7.01
3	$Ti\text{-}/Al_2O_3$	2.35	4.72	1.31	8.12	84.61	1.24	1.99	2.21	7.55
4	Cu/Al_2O_3	2.75	3.75	0.17	8.34	83.78	3.96	2.30	2.64	7.47
5	Pt/MnO_2	1.18	10.37	0.87	19.44	64.19	5.13	0.76	1.05	5.73
6	Cu/MnO_2	1.03	8.66	0.59	21.64	62.84	6.27	0.65	0.93	5.61
7	Pt/ZrO_2	1.98	7.54	0.41	14.35	56.84	20.86	1.13	1.82	5.07
8	Cu/ZrO_2	3.37	9.15	1.71	18.5	51.41	19.23	1.73	3.00	4.59
9	Pt/TiO_2	5.59	3.59	0.68	5.94	84.13	5.66	4.70	5.35	7.50
10	Cu/TiO_2	5.29	0.85	0.19	1.94	95.97	1.05	5.08	5.23	8.56
11	Cu/CeO_2	3.53	13.47	1.58	21.53	58.64	4.78	2.07	2.83	5.23

Condition: catalyst wt.-0.25 g (pallet form); GHSV- 6000 h^{-1}; reaction temp.-350°C; N_2:C_3H_8- 4:1; reaction time-5 hours. The relative standard deviation (RSD) is ±3%.

Table S2 Summary of performance of different catalysts for dehydrogenation of Propane to Propylene

Sl. No	Catalyst	Propane Conv. (%)	Selectivity (%)					Propylene Yield	Total Olefin Yield	Production Rate of Propylene x10^{-7} mmol.g^{-1}.min^{-1})
			CH_4	C_2H_6	C_2H_4	C_3H_6	C_{3+}			
1	TiO_2	5.21	1.83	0.38	3.95	92.36	1.48	4.81	5.02	8.24
2	Cu/TiO_2	8.39	0.66	0.13	1.27	96.65	1.29	8.11	8.22	8.62

Condition: catalyst wt.-0.25 g (pallet form); GHSV- 4000 h^{-1}; reaction temp.-350°C; N_2:C_3H_8- 6:1; reaction time-5 hours. The relative standard deviation (RSD) is ±3%.

Elementary steps taken for DFT study

DFT study was used to understand the propane dehydrogenation (PDH) and possible coking and lights products like CH_4/CH_2CH_2. The following surface mechanism with elementary reaction steps for PDH, coke formation and lights formation as given below,

R1. $CH_3CH_2CH_3 \rightarrow CH_3CH_2CH_2 + H$ (PDH_step1)

R2. $CH_3CH_2CH_2 \rightarrow CH_3CHCH_2 + H$ (PDH_step2)

R3. $CH_3CHCH_2 \rightarrow CH_3CHCH + H$ (coke formation)

R4. $CH_3CH_2CH_2 \rightarrow CH_3CH_2 + CH_2$ (CH_4/CH_2CH_2 formation)

Mass Transfer Calculations for PDH Reaction with Cu/Tio_2 Catalyst

Weisz-Prater Criterion for Internal Diffusion (Elements of Chemical Reaction Engineering, Fogler 5th edition)

If $C_{WP} = \frac{-r'_{A(obs)}\rho_c R^2}{D_e C_{Ps}} < 1$, then internal mass transfer effects can be neglected.

The parameters were determined using the provided formulas. Another option for calculating the internal mass transfer limitation is by performing a theoretical analysis after conducting a preliminary kinetic modeling study, as mentioned in Oyama et al.'s report (reference 21). To estimate the internal mass transfer, the calculation was based on the Weisz-Prater criterion, expressed as follows:

$$C_{WP} = \frac{-r'_{A(obs)}\rho_c R^2}{D_e C_{Ps}}$$

The provided parameters were determined through various calculations:

The reaction rate $r'_{A(obs)}$ in (kmol.kg^{-1}.s^{-1}), dependent on total conversion, reactant flow rate, and catalyst weight, was obtained from kinetic modeling calculations.

The density ρ_c (kg.m^{-3}) of the solid catalyst was experimentally determined by suspending the pelletized catalyst in water.

The average particle radius of the catalyst R (m) was calculated from HR-TEM images.

The effective gas-phase diffusivity D_e (m^2.s^{-1}) for the propane-nitrogen system was appropriately estimated using the Lennard-Jones expression forces and kinetic theory.

C_{Ps} (kmol.m^{-3}) represents the gas concentration of propane (P) at the catalyst surface (s) per unit time.

The detailed calculations for each parameter are provided in the supporting information as follows.

Based on the value of C_{WP}:

If $C_{WP} \ll 1$, the internal mass transfer limitation can be neglected.

If $C_{WP} > 1$, the diffusion behavior significantly affects the overall reaction conversion.

Rate calculation:

$$r'_{A(obs)} = \frac{X_{C_3H_8} . F_{C_3H_8}}{W_{cat.}}$$

$$X_{C_3H_8} = 0.0879$$

$$F_{C_3H_8} = 7.5 \times 10^{-7}\ kmol.s^{-1}$$

$$W_{cat.} = 2.5 \times 10^{-4}\ kg$$

$$r'_{A(obs)} = \frac{X_{C_3H_8} . F_{C_3H_8}}{W_{cat.}} = 2.746 \times 10^{-4}\ kmol.kg^{-1}.s^{-1}$$

Solid catalyst density calculation:

$$\rho_c = \frac{wt\ of\ catalyst}{volume\ displaced\ by\ catalyst} = \frac{0.89}{0.3}\ g.ml^{-1} = 2.96 \times 10^3\ kg.m^{-3}$$

Average particle radius calculation:

Average particle radius of the catalyst was measured from the HR-TEM images of the catalyst.

$$R = 11 \times 10^{-9}\ m$$

Effective gas-phase diffusivity calculation:

$$D_e = \frac{A.T^{3/2}\sqrt{\frac{1}{M_{propane}} + \frac{1}{M_{nitrogen}}}}{\rho.\sigma_{pn}^2.\Omega}$$

A = $1.859 \times 10^{-3} \frac{atm.Å^2.cm^2.\sqrt{g/_{mol}}}{K^{3/2}.s}$

T = 623 K

$M_{propane} = 44$; $M_{nitrogen} = 28$

$\sigma_{pn} = \frac{\sigma_{propane} + \sigma_{nitrogen}}{2}$ = 4.11 Å ; Average collision diameter ($\sigma_{propane}$ = 4.77 Å; $\sigma_{nitrogen}$ = 3.45 Å)

$\Omega \sim 1$; collision integral (dimensionless)

$$D_e = 1.39 \times 10^{-4}\ m^2.s^{-1}$$

Gas concentration of Propane (P) at the catalyst surface (s) calculation:

$C_{Ps} = \frac{0.045\ moles}{0.068\ ml} = 0.66\ moles.ml^{-1} = 11\ kmol.m^{-3}$; molecules of propane interacting at the catalyst surface in per unit time.

Table.S3 Calculated parameters for the Weisz-Prater criterion

Parameters	Value
$-r'_{A(obs)}$	$2.746 \times 10^{-4}\ kmol.kg^{-1}.s^{-1}$
ρ_c	$2.96 \times 10^3\ kg.m^{-3}$
R	$11 \times 10^{-9}\ m$
D_e*	$1.39 \times 10^{-4}\ m^2.s^{-1}$
C_{Ps}	$11\ kmol.m^{-3}$

* Mole-average diffusivity of propane in propane -nitrogen feed mixture

C_{WP} Calclulation:

$$C_{WP} = \frac{-r'_{A(obs)}\rho_c R^2}{D_e C_{Ps}} = \frac{(2.746 \times 10^{-4}) \times (2.96 \times 10^3) \times (11 \times 10^{-9})^2}{(1.39 \times 10^{-4}) \times 11}$$

$$C_{WP} = 6.418 \times 10^{-14} \ll 1$$

The value of the C_{WP} was calculate as 6.418×10^{-14} which was significantly less than 1. Hence, the internal mass transfer limitations can be eliminated.

Mears criterion

$$= \frac{-r'_{A(obs)}R^2}{D_e C_{Ps}} = \frac{(2.746 \times 10^{-4}) \times (11 \times 10^{-9})^2}{(1.39 \times 10^{-4}) \times 11} = 2.17 \times 10^{-17}$$

KINETICS STUDY

The effect of temperature on the reaction rates and product formation over Cu-TiO_2 was investigated at relatively low temperature 350-400 °C using appropriate *W*:*F* ratios to obtain low conversions (<50%). The experimental data was collected after 5h to ensure that a steady state was reached, and stable performance was achieved.

Rate Equations: The numerical values of the conversion, rate and partial pressures are given in the following table. The readings were taken for three temperatures (350, 375 and 400 ˚C) at varying flow rate of N_2 and C_3H_8.

1) T= 350 ^{0}C W$_{cat}$=0.25 g

Propane flow rate (ml/min)	Nitrogen gas flow rate (ml/min)	Partial pressure of propane (atm)	Conversion of Propane (X_{C3H8})	Rate of propane consumption (R_{C3H8}) in mol/g.s
5.55	11.11	0.332197	4.89	0.034875502
3.3	13.3	0.198124	7.31	0.030999161
2.38	14.28	0.142342	8.39	0.025660052

2) T=375 ^{0}C W$_{cat}$= 0.25 g

Propane flow rate (ml/min)	Nitrogen gas flow rate (mL/min)	Partial pressure of propane (atm)	Conversion of Propane (X_{C3H8})	Rate of propane consumption (R_{C3H8}) in mol/g.s
5.55	11.11	0.331482	6.72	0.047784
3.3	13.3	0.197613	8.91	0.037784
2.38	14.28	0.141948	11.4	0.034866

3) T= 400 ^{0}C W$_{cat}$=0.25 g

Propane flow rate (ml/min)	Nitrogen gas flow rate (mL/min)	Partial pressure of propane (atm)	Conversion of Propane (X_{C3H8})	Rate of propane consumption (R_{C3H8}) in mol/g.s
5.55	11.11	0.331398	9.28	0.066185
3.3	13.3	0.197552	12.56	0.053263
2.38	14.28	0.141902	14.26	0.043613

Various rate equations are determined and tested for the reaction.

A. First of all, power law rate equation is assumed.

$R_{C3H8} = k(p_{C3H8})^m$ Equ …………….. (a)

In this equation, R is the rate of propane consumption, p_{C3H8} is the partial pressure of propane and k, m are the constants to be determined.

To determine the constants k and m, a graph between ln R (y axis) and ln p (x axis) is plotted having R as dependent variable and p as independent variable. The graph gives the linear line with slope m and intercept as ln k.

Graphs for the three different temperatures have been shown in Fig. 1 a, b, c.

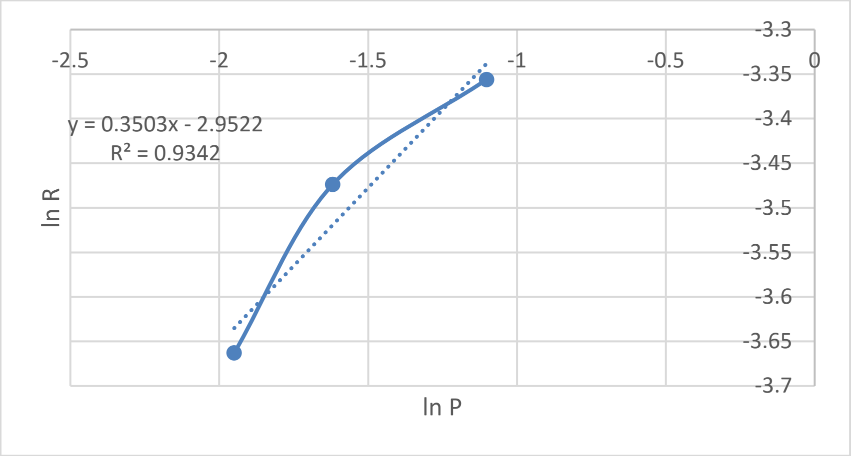


Fig 1 a) T= 350 °C

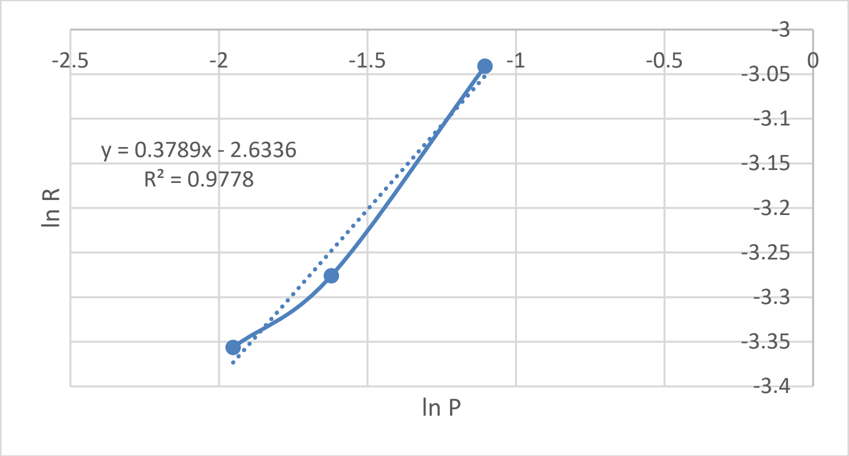


Fig 1 b) T= 375 °C

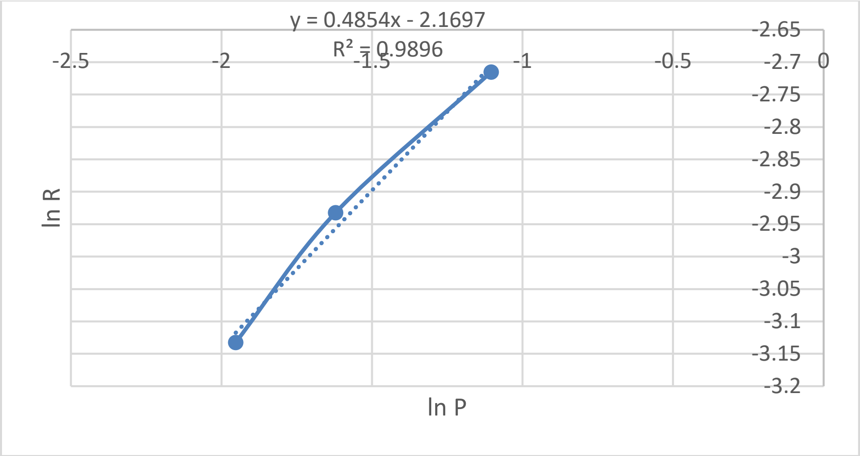


Fig 1 c) T= 400 °C

From these graphs k and m values have been determined and written in the tabular form as follows:

Temperature (°C)	Value of m parameter	k value (μmol/g.s.atm)	Rate expression for Propane
350	0.35027876	0.052224001	R=0.052224*p^0.35027876
375	0.37887895	0.071819396	R=0.071819*p^0.378879
400	0.48543688	0.114217165	R=0.114217*p^0.485437

The catalyst used in this reaction is heterogeneous catalyst. Hence for developing the kinetic equation, we should consider the three steps adsorption, surface reaction and desorption by neglecting the diffusion processes.

Consider the reaction 2P⇔E+H

Where P= propane, E for Propylene and H for Hydrogen

Now we have to propose the mechanism for the reaction. We may consider the following steps occurring throughout the reaction neglecting the internal and external diffusions.

$C_3H_8 + S \Leftrightarrow C_3H_8.S$ (Adsorption step)

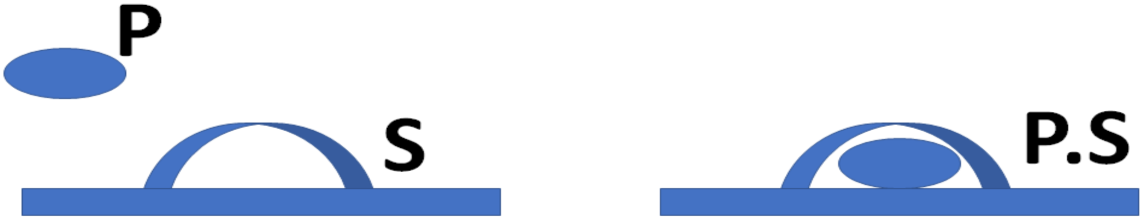
$C_3H_8.S + S \Leftrightarrow C_3H_7.S + H.S$ (Surface reaction steps)

$C_3H_7.S + S \Leftrightarrow C_3H_6.S + H.S$

$C_3H_6.S \Leftrightarrow C_3H_6 + S$ (Desorption step)

$2H.S \Leftrightarrow H_2 + 2S$

Here S represents the vacant site and $C_3H_8.S$, $C_3H_7.S$, $C_3H_6.S$ and H.S represents that the respective species have occupied the site.



This figure represents the vacant site and the occupied sites respectively.

For developing the kinetic equation consider one by one the three steps as the rate limiting step. The slowest step in the reaction is considered as rate limiting step because the whole reaction is governed by that step as other steps are considered to be fast. After the assumption one equation is developed and then that equation is matched with the experimental results.

B) Adsorption as rate limiting step

First consider adsorption as the rate limiting step having the main reaction as
$C_3H_8 + S \Leftrightarrow C_3H_8.S$
Let k_1 and k_{-1} be the rate constants for the forward (adsorption) and backward (desorption) reactions. Then rate of propane adsorption is given by $r_A = k_1.S_v.P_{C3H8}$ and methanol desorption is $r_{-1} = k_{-1}.S_{C3H8.S}$ where S_v and $S_{C3H8.S}$ are the concentrations of the vacant sites and the occupied sites respectively. Combining these two equations we get the net rate of adsorption as $R_A = k_1.S_V.P_{C3H8} - k_{-1}.S_{C3H8.S}$
Solving this equation, we get $R_A = k_1\left(S_V.P_{C3H8} - \frac{k_{-1}.C_{C3H8.S}}{k_1}\right)$
$R_A = k_1\left(S_v.P_{C3H8} - \frac{S_{C3H8.S}}{\boldsymbol{K_A}}\right)$.....................................(A)
where $K_A = k_1/k_{-1}$ and is known as equilibrium constant. This equation is also known as Langmuir adsorption isotherm.
Now surface reaction and desorption steps are very fast so consider their rates to be zero.
Surface reaction is $C_3H_8.S + S \Leftrightarrow C_3H_7.S + H.S$ and let k_2 and k_{-2} be the rate constants for forward and backward reactions. Then $R_{S1} = k_2.S_{C3H8.S}S_S - k_{-2}.S_{C3H7.S}.S_{H.S}$ or $k_2(S_{C3H8}S_S - \frac{k_{-2}.S_{C3H7.S}.S_{H.S}}{k_2})$
$R_{S1} = k_2\left(S_{C3H8.S}S_S - \frac{S_{C3H7.S}.S_{H.S}}{K_{S1}}\right)$ where $K_{S1} = k_2/k_{-2}$
Putting R_{S1}=0 and solving we get $S_{C3H8.S} = \frac{S_{C3H7.S}.S_{H.S}}{K_{S1}.S_S}$ ....(1)
Similarly, for the second surface reaction step
$C_3H_7.S + S \Leftrightarrow C_3H_6.S + H.S$
let k_3 and k_{-3} be the rate constants for forward and backward reactions. Then
$R_{S2} = k_3.S_{C3H7.S}S_S - k_{-3}.S_{C3H6.S}.S_{H.S}$ or $k_3(S_{C3H7.S}S_S - \frac{k_{-3}.S_{C3H6.S}.S_{H.S}}{k_3})$
$R_{S2} = k_3\left(S_{C3H7.S}S_S - \frac{S_{C3H6.S}.S_{H.S}}{K_{S2}}\right)$ where $K_{S2} = k_3/k_{-3}$
Putting R_{S2}=0 and solving we get $S_{C3H7.S} = \frac{S_{C3H6.S}.S_{H.S}}{K_{S2}.S_S}$ ....(2)

Consider the desorption reaction $C_3H_6.S \Leftrightarrow C_3H_6 + S$ and let k_4 and k_{-4} be the rate constants for forward and backward reactions. Then similarly
$R_{D1} = k_4.S_{C3H6.S} - k_{-4}.P_{C3H6}.S_S$
$R_{D1} = k_4\left(S_{C3H6.S} - \frac{P_{C3H6}.S_S}{K_{D1}}\right)$where $K_D = k_4/k_{-4}$
Putting $R_{D2} \approx 0$, we get $S_{C3H6.S} = \frac{P_{C3H6}.S_S}{K_{D1}}$...(3)
Similarly for the second desorption reaction $2H.S \Leftrightarrow H_2 + 2S$ and let k_5 and k_{-5} be the rate constants for forward and backward reactions. Then similarly
$R_{D2} = k_5.S_{H.S}{}^2 - k_{-5}.P_{H2}.S_S{}^2$
$R_{D2} = k_5.(S_{H.S}{}^2 - \frac{P_{H2}.S_S{}^2}{K_{D2}})$where $K_{D2} = k_5/k_{-5}$
Putting $R_{D2} \approx 0$, we get $S_{H.S} = \sqrt{\frac{P_{H2}.}{K_{D2}}}.S_{S.}$ ....(4)
Total site balance can be written as
$S_t = S_v + S_{C3H7.S} + S_{C3H6.S} + S_{H.S} + S_S$
Replacing each of the above values from equations (1), (2), (3) and (4) we get

$$S_t = \left(\frac{S_{C3H7.S}.S_{H.S}}{K_{S1}.S_S} + \frac{S_{C3H6.S}.S_{H.S}}{K_{S2}.S_S} + \frac{P_{C3H6}.S_S}{K_{D1}} + \sqrt{\frac{P_{H2}}{K_{D2}}}.S_S + S_S\right)$$

$$S_t = \left(\frac{S_{C3H7.S}.S_{H.S}{}^2}{K_{S1}.S_S{}^2.K_{S2}} + \frac{P_{C3H6}.S_{H.S}.S_S}{K_{S2}.S_S.K_{D1}} + \frac{P_{C3H6}.S_S}{K_{D1}} + \sqrt{\frac{P_{H2}}{K_{D2}}}.S_S + S_S \right)$$

$$S_t = \left(\frac{P_{C3H6}.S_{H.S}{}^2.S_S}{K_{S1}.S_S{}^2.K_{S2}.K_{D1}} + \frac{P_{C3H6}.P_{H2}{}^{1/2}.S_S}{K_{S2}.K_{D2}{}^{1/2}.K_{D1}} + \frac{P_{C3H6}.S_S}{K_{D1}} + \sqrt{\frac{P_{H2}}{K_{D2}}}.S_S + S_S \right)$$

$$S_t = \left(\frac{P_{C3H6}.P_{H2}.S_S}{K_{S1}.K_{D2}.K_{S2}.K_{D1}} + \frac{P_{C3H6}.P_{H2}{}^{1/2}.S_S}{K_{S2}.K_{D2}{}^{1/2}.K_{D1}} + \frac{P_{C3H6}.S_S}{K_{D1}} + \sqrt{\frac{P_{H2}}{K_{D2}}}.S_S + S_S \right)$$

$$S_t = \left[\left(\frac{P_{C3H6}.P_{H2}}{K_{S1}.K_{D2}.K_{S2}.K_{D1}} \right) + \frac{P_{C3H6}.P_{H2}{}^{1/2}}{K_{S2}.K_{D2}{}^{1/2}.K_{D1}} + \frac{P_{C3H6}}{K_{D1}} + \sqrt{\frac{P_{H2}}{K_{D2}}} + 1 \right].S_S$$

$$S_S = \frac{S_t}{\left(\frac{P_{C3H6}.P_{H2}}{K_{S1}.K_{D2}.K_{S2}.K_{D1}} \right) + \frac{P_{C3H6}.P_{H2}{}^{1/2}}{K_{S2}.K_{D2}{}^{1/2}.K_{D1}} + \frac{P_{C3H6}}{K_{D1}} + \sqrt{\frac{P_{H2}}{K_{D2}}} + 1}$$

Substituting equations (5) and (1) in equation (A), we get

$$R_A = k_1 \left(S_S.P_{C3H8} - \frac{P_{C3H6}.P_{H2}.S_S}{K_{S1}.K_{D2}.K_{S2}.K_{D1}} \right)$$

$$R_A = \frac{k_1.S_t}{\left(\frac{P_{C3H6}.P_{H2}}{K_{S1}.K_{D2}.K_{S2}.K_{D1}} \right) + \frac{P_{C3H6}.P_{H2}{}^{1/2}}{K_{S2}.K_{D2}{}^{1/2}.K_{D1}} + \frac{P_{C3H6}}{K_{D1}} + \sqrt{\frac{P_{H2}}{K_{D2}}} + 1}.\left(P_{C3H8} - \frac{P_{C3H6}.P_{H2}}{K_{S1}.K_{D2}.K_{S2}.K_{D1}} \right)$$

Considering P_{C3H6} *and* P_{H2} as zero for initial kinetics,
$R_A = k_1.S_t.P_{C3H8}$
$R_A = K_1.P_{C3H8}$ where $K_1 = k_1.S_t$
Using this equation, we can plot between Rate and partial pressure of propane at different temperatures to find the value of k.
Graphs at these temperatures are given below.

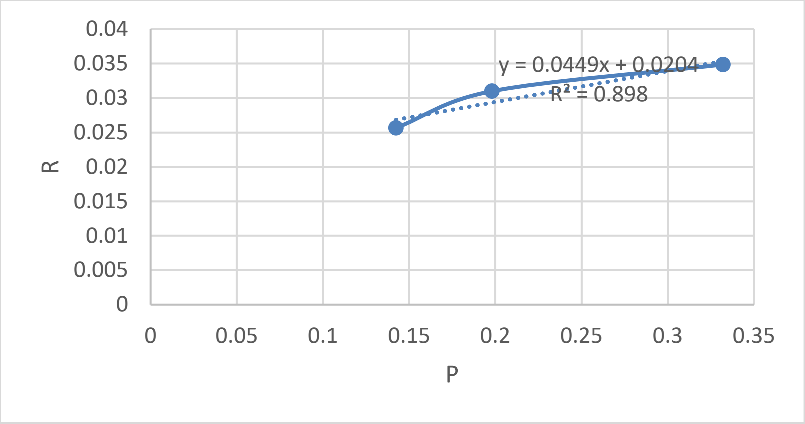


Fig 2 a) T=350 °C

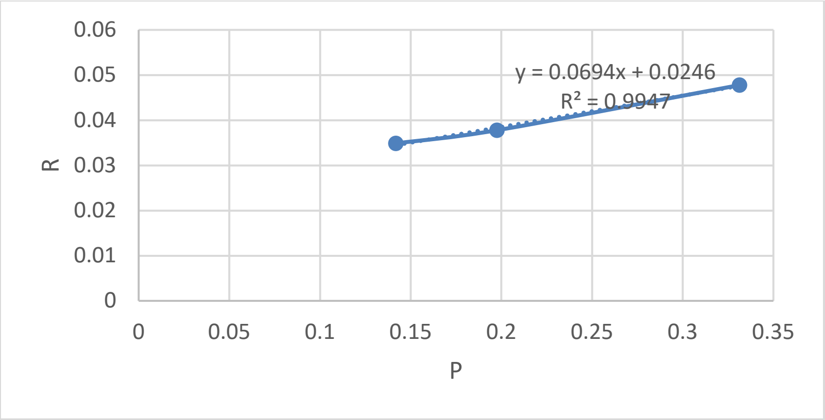


Fig 2 b) T= 375 °C

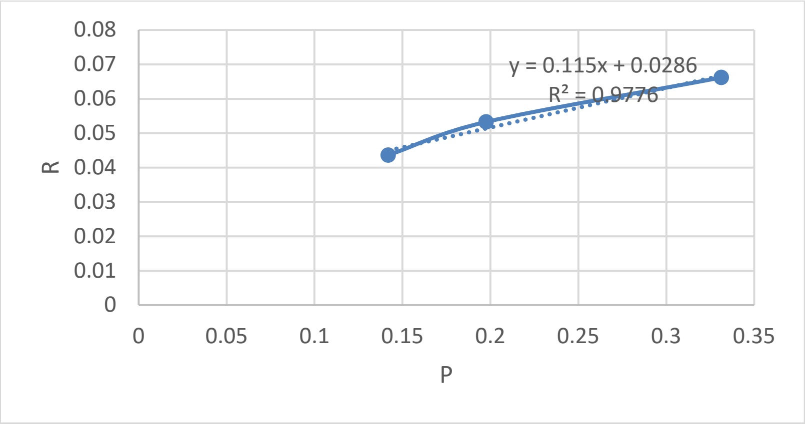


Fig 2 c) T= 400 °C

From these graphs the evaluated k values are represented in table as follows:

Temperature (^{0}C)	Value of k (µmol/g.s.atm)	Rate equation
350	0.044933325	R=0.0442*p
375	0.06936238	R=0.1876*p
400	0.114966586	R=0.3111*p

C) Surface Reaction 1 as rate limiting step

Consider the surface reaction as $C_3H_8.S + S \Leftrightarrow C_3H_7.S + H.S$
Then $R_{S1} = k_2.S_{C3H8.S} - k_{-2}.S_{C3H7.S}.S_{H.S}$
Or $R_{S1} = k_2\left(S_{C3H8.S} - \frac{1}{K_{S1}}.S_{C3H7.S}.S_{H.S}\right)$
From adsorption step,
$P_{C3H8}S_S = \frac{S_{C3H8.S}}{K_A}$

$S_{C3H8.S} = K_A.S_S P_{C3H8}$

$S_{C3H8.S} = S_S \frac{P_{C3H6} P_{H2}^{1/2}}{K_{S2}.K_{D2}.K_{D1}}$

$S_{H.S} = S_S.\frac{P_{H2}^{1/2}}{K_{D2}^{1/2}}$

Therefore, $R_{S1} = k_2 \left(K_A.S_S^2 P_{C3H8} - \frac{P_{C3H6}\ P_{H2}}{K_{S2}K_{D1}K_{D2}^{3/2}} S_S^2\right)$

From total sites,

$$S_t = \left(K_A.P_{C3H8}.S_S + S_S \frac{P_{C3H6.}.P_{H2}^{1/2}}{K_{S2}.K_{D2}.K_{D1}} + \frac{P_{C3H6}.S_S}{K_{D1}} + \sqrt{\frac{P_{H2}}{K_{D2}}} S_S + S_S\right)$$

$$S_t = \left(K_A.P_{C3H8} + \frac{P_{C3H6.}.P_{H2}^{1/2}}{K_{S2}.K_{D2}.K_{D1}} + \frac{P_{C3H6}}{K_{D1}} + \sqrt{\frac{P_{H2}}{K_{D2}}} + 1\right).S_S$$

$$R_{S1} = \frac{K_2.S_t^2}{\left(K_A.P_{C3H8} + \frac{P_{C3H6.}.P_{H2}^{1/2}}{K_{S2}.K_{D2}.K_{D1}} + \frac{P_{C3H6}}{K_{D1}} + \sqrt{\frac{P_{H2}}{K_{D2}}} + 1\right)^2} \left(K_A.P_{C3H8} - \frac{P_{C3H6}\ P_{H2}}{K_{S2}K_{D1}K_{D2}^{3/2}}\right)$$

Considering P_{C3H6} *and* P_{H2} as zero for initial kinetics,

$R_{S1} = \frac{K_2.S_t^2.K_A.P_{C3H8}}{(K_A.P_{C3H8}+1)^2}$ OR $R_{S1} = \frac{k.K_A.P_{C3H8}}{(K_A.P_{C3H8}+1)^2}$ where k= $K_2.S_t^2$

Parameters k and K_M of these equations are estimated by non-linear regression analysis minimizing the sum of the squared differences of calculated and experimental CH_4 reforming rates using the Levenberg–Marquardt algorithm provided in the computer software POLYMATH 5.1 environment.

Polymath results for all three temperatures are given below:

Temperature (°C)	k (μmol^2/g^2.s)	K_A (1/atm)	Rate equation
350	0.1436872	2.20326	$R_{S1} = 0.1436872 \frac{2.20326.P_{C3H8}}{(K_A.P_{C3H8}+1)^2}$
375	0.198852	1.917504	$R_{S1} = 0.198852 \frac{1.917504.P_{C3H8}}{(K_A.P_{C3H8}+1)^2}$
400	0.2948139	1.560042	$R_{S1} = 0.2948139 \frac{1.560042.P_{C3H8}}{(K_A.P_{C3H8}+1)^2}$

D) Surface Reaction 2 as rate limiting step

Consider the surface reaction as $C_3H_7.S + S \Leftrightarrow C_3H_6.S + H.S$

Then $R_{S2} = k_3.S_{C3H7.S}S_S - k_{-3}.S_{C3H6.S}.S_{H.S}$

Or $R_{S2} = k_3 \left(S_{C3H7.S}S_S - \frac{1}{K_{S2}}.S_{C3H6.S}.S_{H.S}\right)$ where $K_{S2} = k_3/k_{-3}$

From adsorption step,

$K_A P_{C3H8} S_S = \frac{S_{C3H7.S}\ .\ S_{H.S}}{K_{S1} S_S} = \frac{S_{C3H7.S}}{K_{S1}} \frac{P_{H2}^{1/2}}{K_{D2}^{1/2}}$

$S_{C3H7.S} = \frac{K_{D2}^{1/2}.K_A.S_S.P_{C3H8}}{P_{H2}^{1/2}}$

$S_{C3H6.S} = S_S \frac{P_{C3H6}}{K_{D1}}$

$$S_{H.S} = S_S.\frac{P_{H2}^{\ 1/2}}{K_{D2}^{\ 1/2}}$$

Therefore, $R_{S2} = k_3\left(\frac{K_A.K_{S1}.K_{D2}^{\ 1/2}.P_{C3H8}}{P_{H2}^{\ 1/2}}.S_S^{\ 2} - \frac{P_{C3H6}\ P_{H2}^{\ 1/2}}{K_{S2}K_{D1}K_{D2}^{\ 1/2}}S_S^{\ 2}\right)$

$$R_{S2} = k_3.S_S^{\ 2}\left(\frac{K_A.K_{S1}.K_{D2}^{\ 1/2}.P_{C3H8}}{P_{H2}^{\ 1/2}}.-\frac{P_{C3H6}\ P_{H2}^{\ 1/2}}{K_{S2}K_{D1}K_{D2}^{\ 1/2}}\right)$$

It is obvious from the experimental data that this equation does not fits to the reaction kinetics.

E) C_3H_6 DESORPTION as rate limiting step

Consider the desorption reaction as $C_3H_6.S \Leftrightarrow C_3H_6 + S$

Then $R_{D1} = k_4.S_{C3H6} - k_{-4}.P_{C3H6}.S_S$

Or $R_{D1} = k_4\left(S_{C3H7.S} - \frac{1}{K_{D1}}.P_{C3H6}.S_S\right)$ where $K_{D1} = k_4/k_{-4}$

From adsorption step,

$$S_{C3H8} = K_A P_{C3H8}.S_S$$

$$\frac{S_{C3H7.S}\cdot\ S_{H.S}}{K_{S1}.S_S} =. K_A.S_{S.}P_{C3H8}$$

$$\frac{S_{C3H6.S}\cdot\ S_{H.S}^{\ 2}}{K_{S1}.K_{S2}.S_S^{\ 2}} =. K_A.S_{S.}P_{C3H8}$$

$$S_{C3H6.S} = K_{S1}.K_{S2}.K_A.S_S^{\ 3}P_{C3H8}$$

$$S_{C3H6.S} = K_{S1}.K_{S2}K_A S_S K_{D2}\frac{P_{C3H8}}{P_{H2}}$$

Therefore, $R_{D1} = k_4\left(\frac{K_A.K_{S1}.K_{S2}.P_{C3H8}}{P_{H2}^{\ 1/2}} - \frac{P_{C3H6}}{K_{D1}}\right)$

$$R_{S2} = k_3.S_S^{\ 2}\left(\frac{K_A.K_{S1}.K_{D2}^{\ 1/2}.P_{C3H8}}{P_{H2}^{\ 1/2}}.-\frac{P_{C3H6}\ P_{H2}^{\ 1/2}}{K_{S2}K_{D1}K_{D2}^{\ 1/2}}\right).S_S$$

$$S_t = \left(P_{C3H8}.K_A.S_S + \frac{K_A.K_{S1}.P_{C3H8}.K_{D2}^{\ 1/2}S_S}{P_{H2}^{\ 1/2}} + \frac{K_A.K_{S1}.P_{C3H8}.S_S}{P_{H2}} + \sqrt{\frac{P_{H2}}{K_{D2}}}.S_S + S_S\right)$$

$$S_S = \frac{S_t}{P_{C3H8}.K_A + \frac{K_A.K_{S1}.P_{C3H8}.K_{D2}^{\ 1/2}}{P_{H2}^{\ 1/2}} + \frac{K_A.K_{S1}.P_{C3H8}}{P_{H2}} + \sqrt{\frac{P_{H2}}{K_{D2}}} + 1}$$

It is obvious from the experimental data that this equation does not fits to the reaction kinetics.

F) H_2 DESORPTION as rate limiting step

Consider the desorption reaction as $2H.S \Leftrightarrow H_2 + 2S$

Then $R_{D2} = k_5.S_{H2} - k_{-5}.P_{H2}.S_S^{\ 2}$

Or $R_{D2} = k_5\left(S_{H2}^{\ 2} - \frac{1}{K_{D2}}.P_{H2}.S_S^{\ 2}\right)$ where $K_{D2} = k_5/k_{-5}$

From adsorption step,

$$S_{C3H8} = K_A P_{C3H8}.S_S$$

$$\frac{S_{C3H7.S}\cdot\ S_{H.S}}{K_{S1}.S_S} =. K_A.S_{S.}P_{C3H8}$$

$$\frac{S_{C3H6.S}\cdot\ S_{H.S}^{\ 2}}{K_{S1}.K_{S2}.S_S^{\ 2}} =. K_A.S_{S.}P_{C3H8}$$

$$\frac{P_{C3H6..}\,S_{H.S}{}^{2}}{K_{D1}.K_{S1}.K_{S2}} = K_A.S_S{}^{2}P_{C3H8}$$

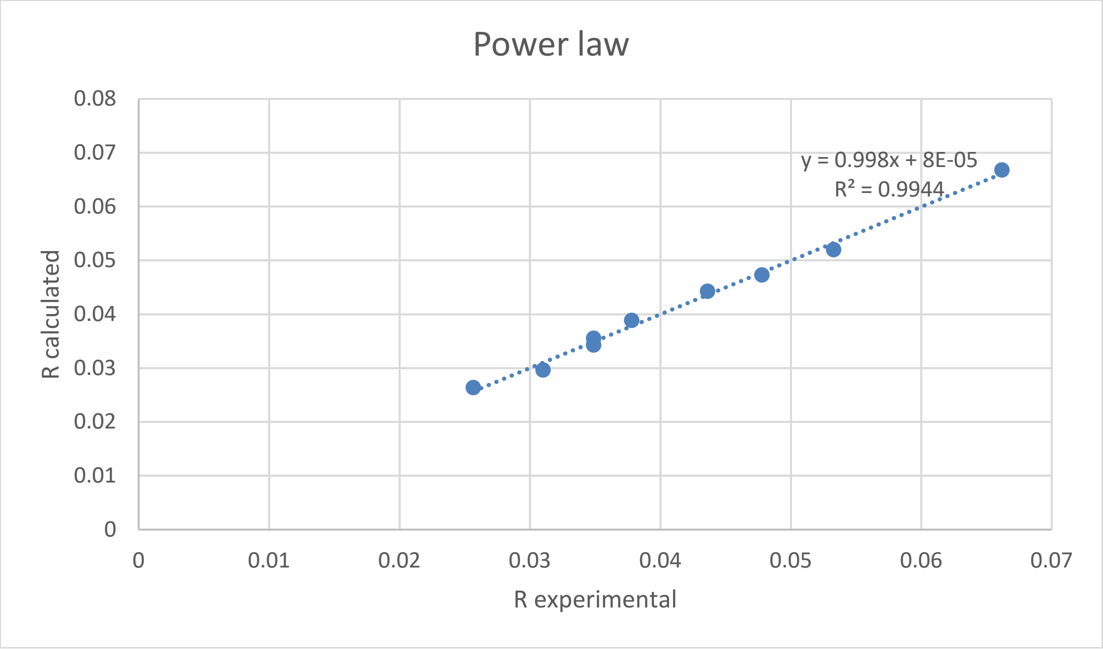
$$S_{H.S}{}^{2} = K_{S1}.K_{S2}.K_{D1}.K_A.S_S{}^{2}\frac{P_{C3H8}}{P_{C3H6}}$$

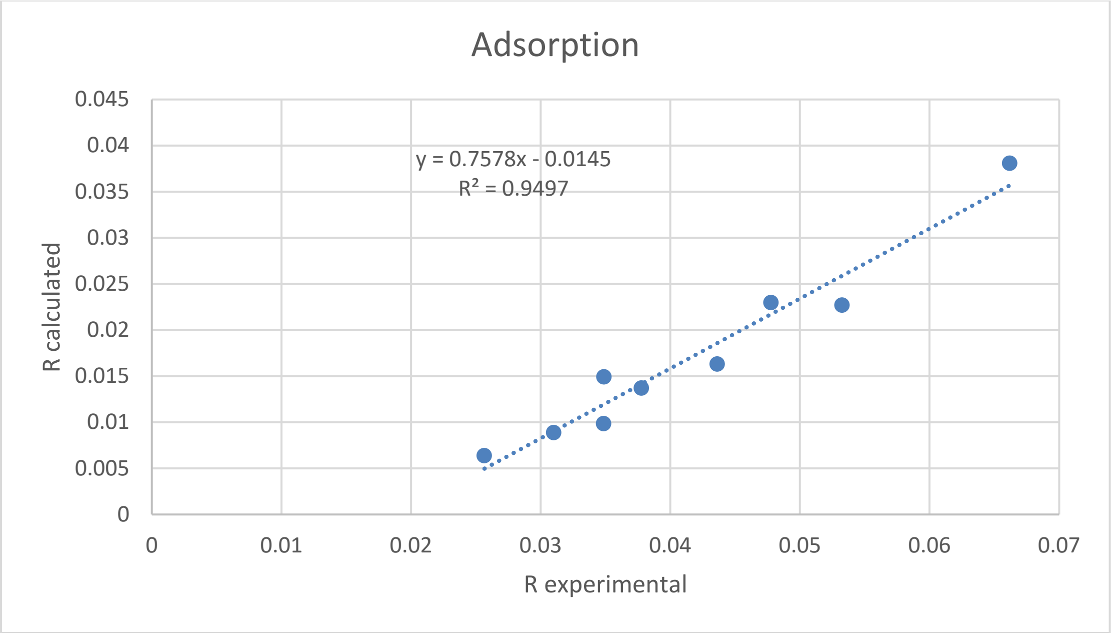
Therefore, $R_{D2} = k_5.S_S{}^{2}.\left(\frac{K_A.K_{S1}.K_{S2}.K_{D1}.P_{C3H8}}{P_{C3H6}} - \frac{P_{H2}}{K_{D2}}\right)$

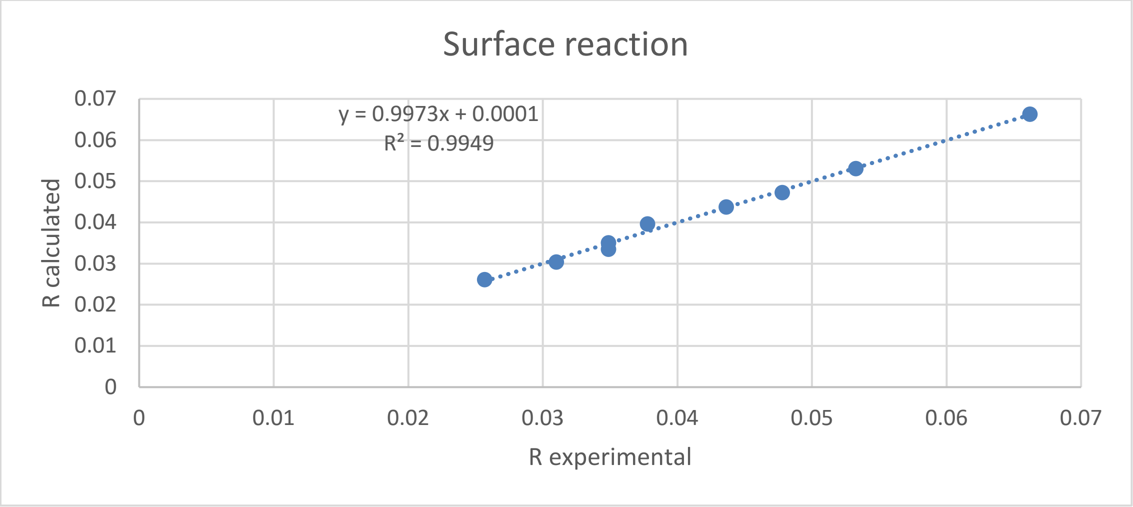
It is obvious from the experimental data that this equation does not fits to the reaction kinetics. Using these expressions $R_{calculated}$ have been evaluated and are tabulated with $R_{observed}$ as follows:

$R_{observed}$	$R_{calculated}$ (Power law rate equation)	$R_{calculated}$ (Adsorption as rate limiting step)	$R_{calculated}$ (Surface reaction as rate limiting)
0.025660052	0.026381545	0.006395834	0.02611434
0.030999161	0.029621185	0.008902323	0.030394758
0.034865864	0.034276739	0.009845831	0.033442231
0.034875502	0.035499747	0.014926613	0.035061115
0.037784203	0.038854241	0.013706816	0.039627897
0.043612914	0.044266469	0.016314069	0.043749837
0.04778443	0.04726633	0.02299228	0.047245724
0.05326258	0.051979125	0.022712016	0.053091497
0.066185001	0.066817607	0.038099849	0.066231715

The graphs between the calculated and observed values are shown in the figures.







It is clear from the graph that adsorption reaction rate limiting step is the best fit mechanism for the dehydrogenation of propane. Also, it is heterogeneous reaction, hence adsorption reaction limiting model is superior to power law rate equation (generally used for homogeneous catalyst).

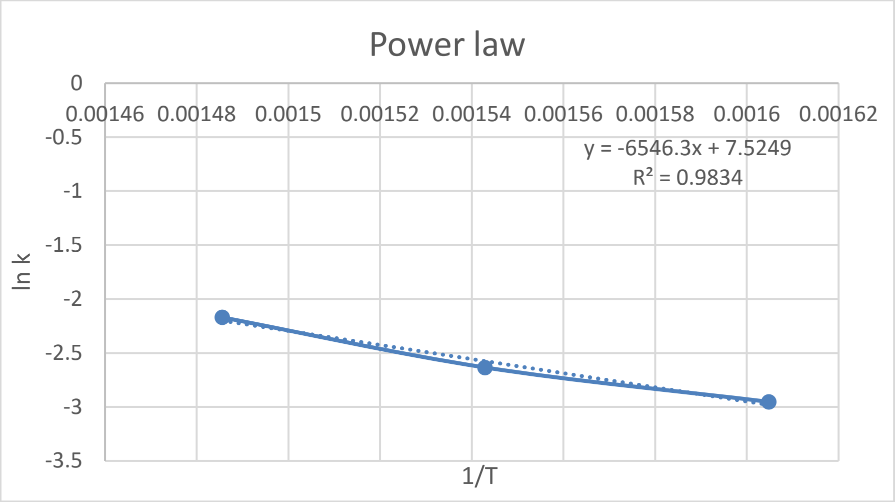
ACTIVATION ENERGY

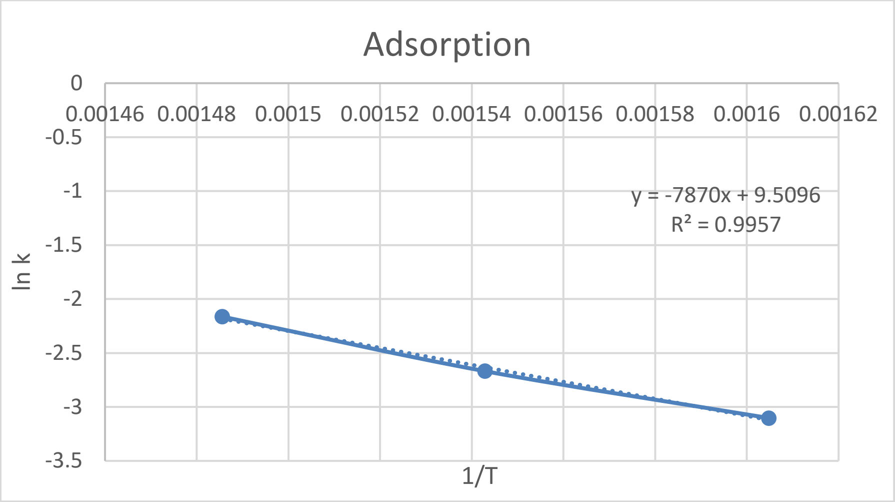
Activation energy for the Propane dehydrogenation process is found by using the Arrhenius equation.

$$k = k_0 e^{\frac{-E}{RT}}$$

A plot between ln k and 1/T is plotted having the slope –E/R and intercept as ln k_0

Activation energies have been evaluated for the power law rate equation, adsorption as rate limiting and surface reaction as rate limiting steps. Their graphs and tables are shown below:


Power law
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
0.00146
0.00148
0.0015
0.00152
0.00154
0.00156
0.00158
0.0016
0.00162
ln k
1/T
y = -6546.3x + 7.5249
R² = 0.9834


Adsorption
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
0.00146
0.00148
0.0015
0.00152
0.00154
0.00156
0.00158
0.0016
0.00162
ln k
1/T
y = -7870x + 9.5096
R² = 0.9957

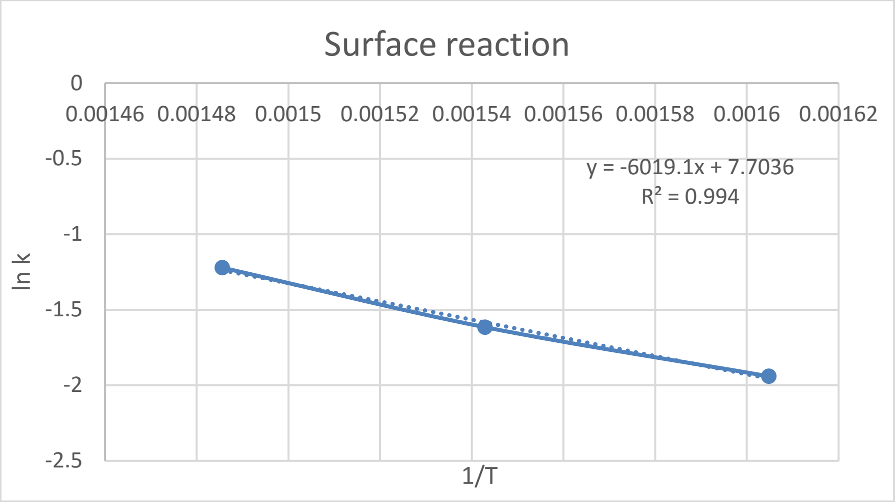

Surface reaction
0
-0.5
-1
-1.5
-2
-2.5
0.00146
0.00148
0.0015
0.00152
0.00154
0.00156
0.00158
0.0016
0.00162
ln k
1/T
y = -6019.1x + 7.7036
R² = 0.994

Table.S3 Derived Activation energy and Arrhenius constant

Rate Expression	Activation energy	Arrhenius constant
$R_{S1} = \frac{k.K_A.P_{C3H8}}{(K_A.P_{C3H8} + 1)^2}$	50.04147 KJ/mole	2216.398
$R_A = K_1.P_{C3H8}$	65.42903 KJ/mole	13488.96
$R_{C3H8} = k(p_{C3H8})^m$	54.42437 KJ/mole	1853.641

From these three equations the graph fitted to the experimental data is adsorption rate limiting step. Hence by using the Arrhenius plot of the surface reaction rate limiting mechanism the activation energy for the reaction is found to be 50.04147 KJ/mole.