Elucidating the impact of oxygen on the kinetic assessment of the oxidative dehydrogenation of ethane on a NiO-SnO$_2$ catalyst .

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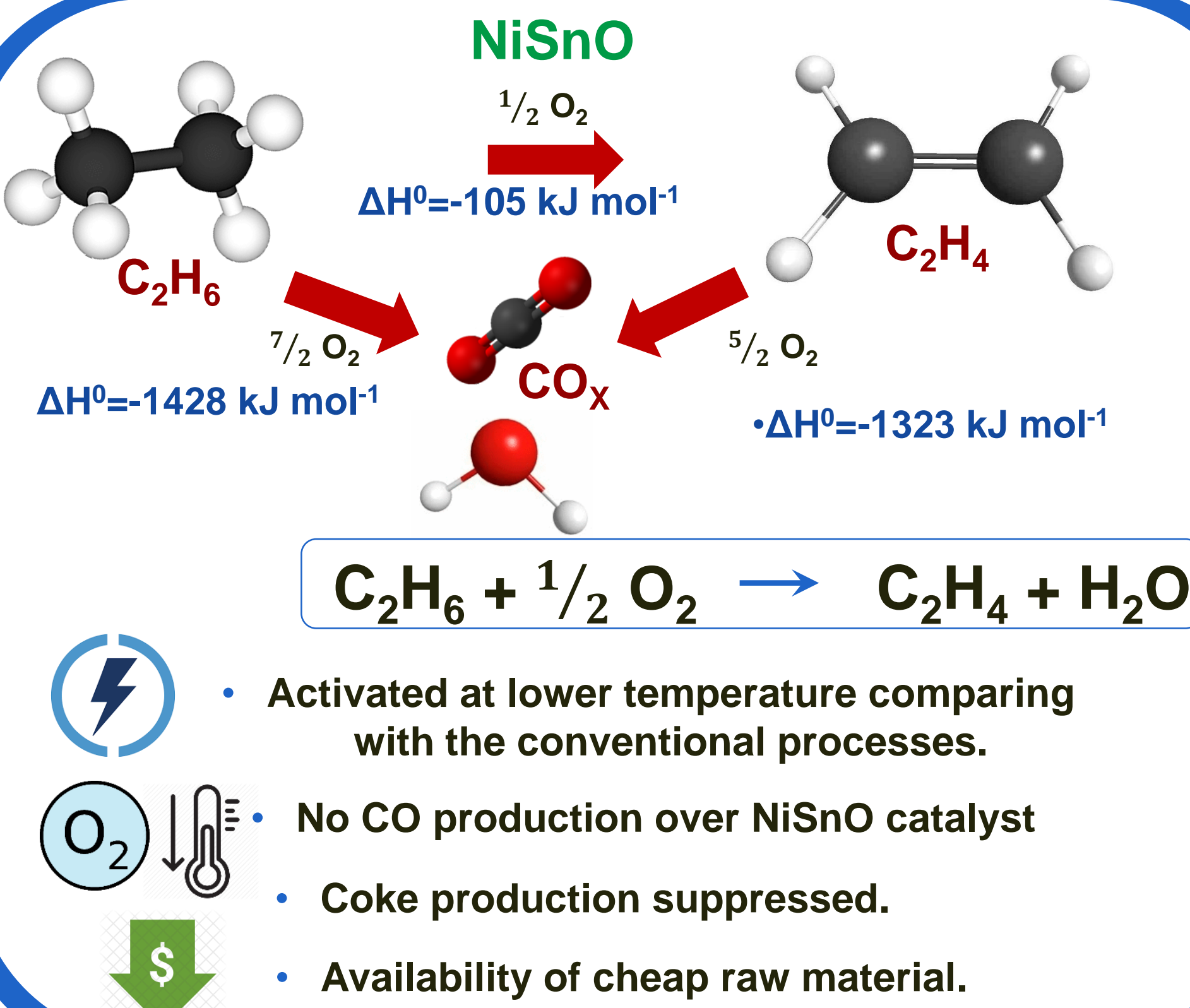http://www.iztapalapa.uam.mx

INTRODUCTION

- Ethylene is an important building block in chemical industry.
- Current industrial processes (steam cracking, FCC and catalytic dehydrogenation) exhibit a set of drawbacks.[1,2]
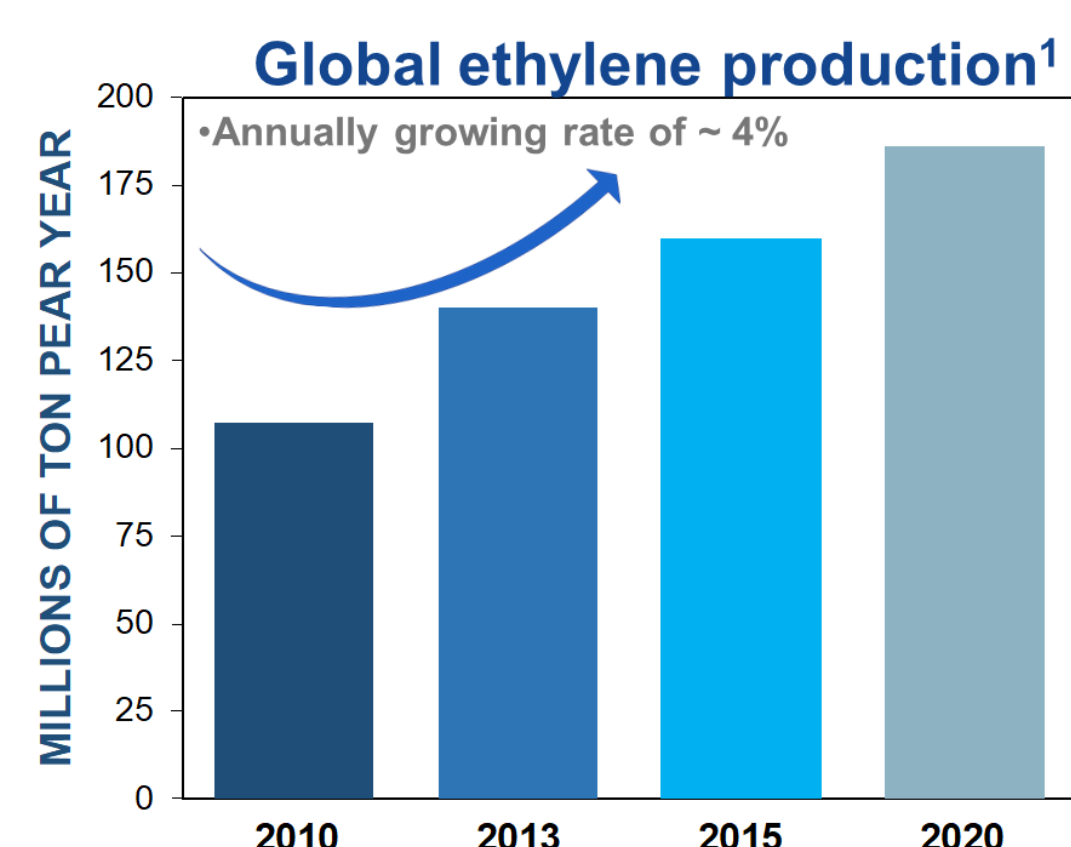
⚠️
  - Thermodynamic limitations
  - High energy requirements
  - Catalyst deactivation
  - Product separation
  - High production of CO$_x$.

Global ethylene production[1]
Annually growing rate of ~ 4%
(Millions of ton pear year vs 2010, 2013, 2015, 2020)

- The ever increasing ethylene demand and environmental requirements have lead to search of new processes to convert light hydrocarbons into more valuable products.

OXIDATIVE DEHYDROGENATION OF ETHANE

NiSnO

C_2H_6 → (½ O$_2$) → C_2H_4
$\Delta H^0 = -105$ kJ mol^{-1}

C_2H_6 + $\frac{7}{2}$ O$_2$ → CO$_x$, $\Delta H^0 = -1428$ kJ mol^{-1}

C_2H_4 + $\frac{5}{2}$ O$_2$ → CO$_x$, $\Delta H^0 = -1323$ kJ mol^{-1}

$$C_2H_6 + \tfrac{1}{2} O_2 \longrightarrow C_2H_4 + H_2O$$

- Activated at lower temperature comparing with the conventional processes.
- No CO production over NiSnO catalyst
- Coke production suppressed.
- Availability of cheap raw material.

METHODOLOGY

Catalyst synthesis — **Evaporation method[4]**

Ni(NO$_3$)$_2$•6H$_2$O + H$_2$C$_2$O$_4$ + SnC$_2$O$_4$
T = 60 °C → T = 500 °C 2 h

- **Experimental kinetic study**

Experimental conditions

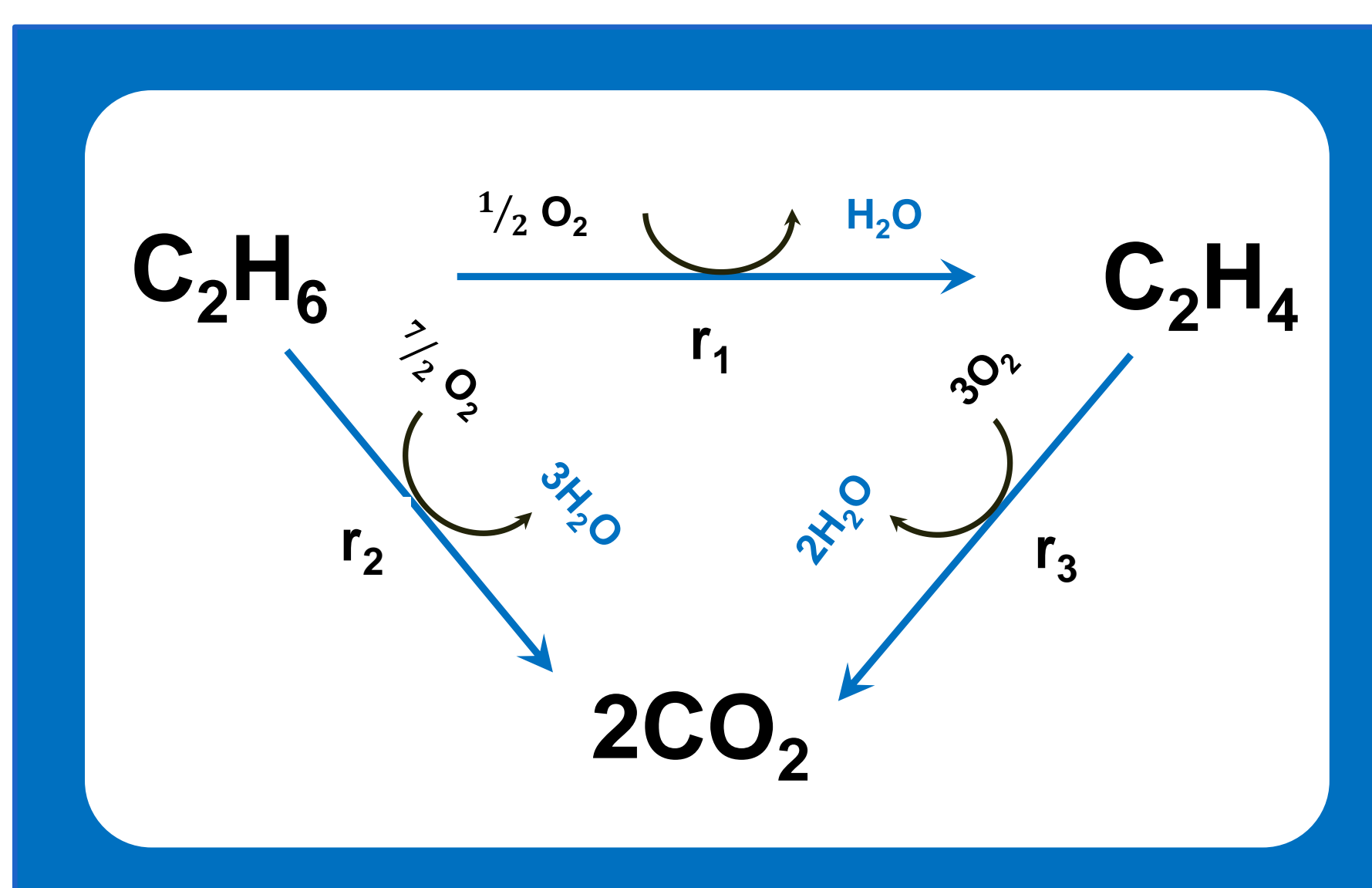| Ranges	
Temperature	350 – 480 °C
Oxygen concentration	1.8 – 9 %mol$_{O2}$
Total Pressure	1 - 5 bar
Ethane concentration	7 - 9 %mol$_{C2}$
W$_{cat}$/F$_{C2H6o}$	9 – 165 kg$_{cat}$ s/ mol$_{C2H6o}$
Catalyst mass	0.075 g to 0.5 g

Set of 111 experiments
Intrinsic kinetic measurements

GENERAL CONSIDERATIONS

- Experiments were performed under two oxygen conversion regimes, one dataset involving 51 experiments at non-total oxygen conversion and a second dataset accounting for 60 observations at total oxygen conversion.
- Parallel-consecutive reaction network is considered.
- Catalyst consists of one type active site (*) with two functionalities.
- The models were developed assuming the steady state approach.
- Competitive adsorption of reactants (ethane and oxygen) and products (ethylene, carbon oxides and water) on the active sites was considered.
- Taking account thermodynamics surface reactions are considered irreversible.
- All products are susceptible to be re-adsorbed on the active sites.
- **According with the rate equations, the model does not consider an specific rate determining step.**

KINETIC MODEL CONSTRUCTION AND RESULTS

C_2H_6 → (½ O$_2$, H$_2$O, r$_1$) → C_2H_4
C_2H_6 → (½ O$_2$, 3H$_2$O, r$_2$) → 2CO$_2$
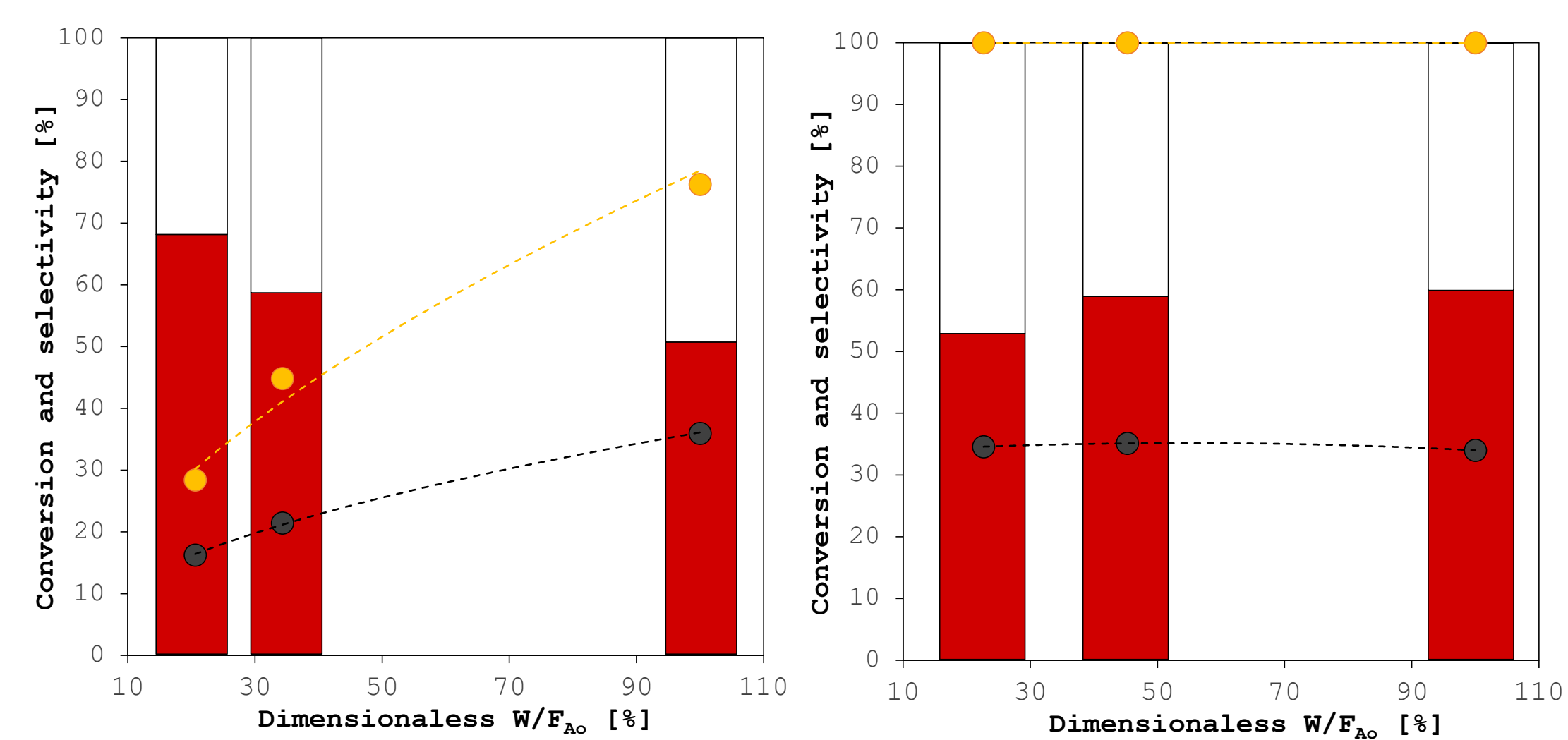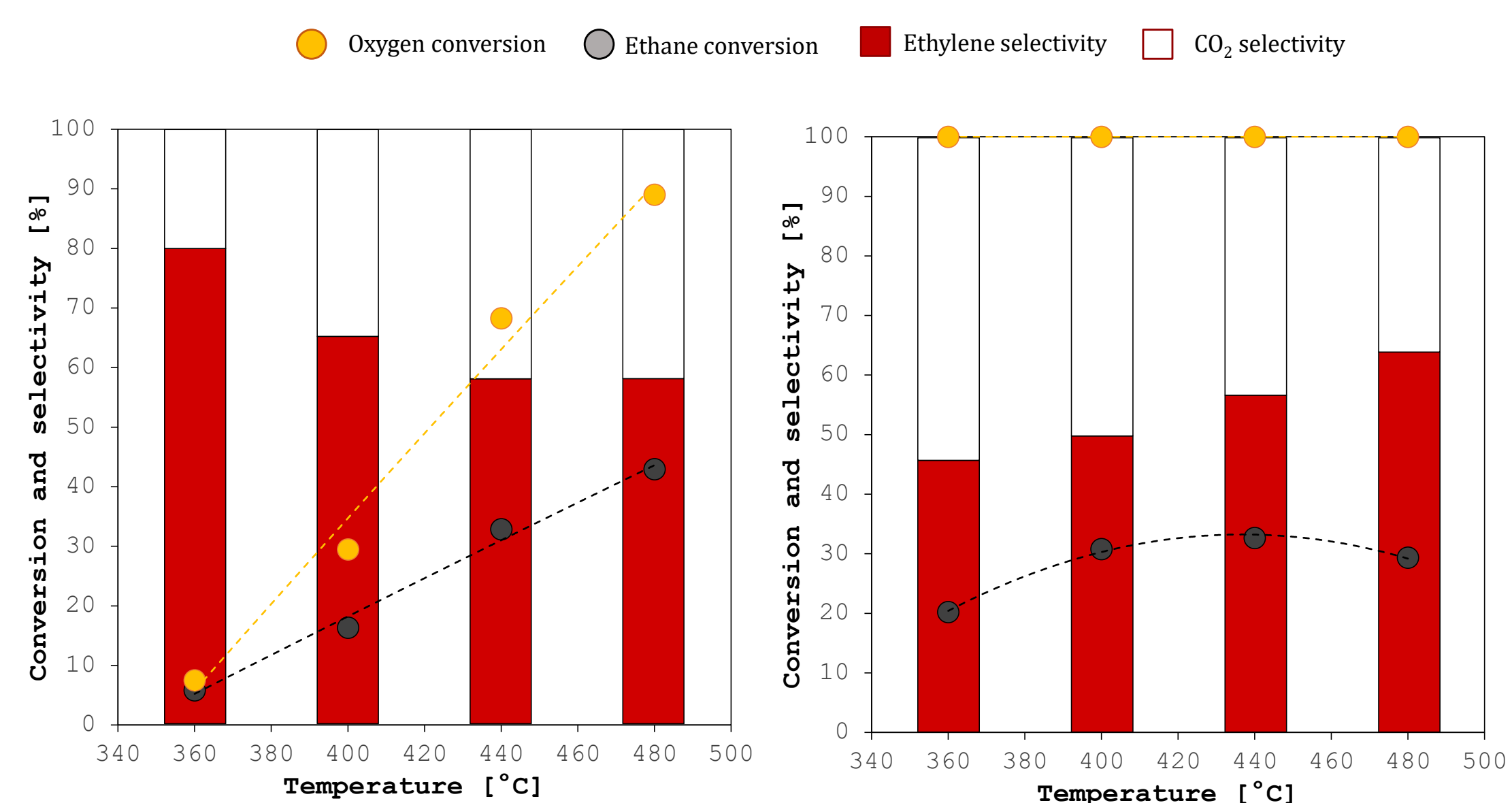C_2H_4 → (2H$_2$O, 3O$_2$, r$_3$) → 2CO$_2$

MODEL COMPARISON AND DISCUSSION

- For both experimental sets, the estimated activation energies increase in the following order: Ea$_{,1}$ < Ea$_{,2}$ < Ea$_3$, the total oxidation reaction requires more energy to be carried out.
- The most sensitive reaction activation energy is for the total oxidation of ethylene (Ea$_3$),the one estimated with the total oxygen conversions is ≈20 kJ/mol higher than those estimated with the other experimental set.
- For both models, the best fit by species is for ethane and ethylene.
- According to the values of the adsorption enthalpies and the concentration of adsorbed species on the surface, depending of the experimental set used, the adsorbed species distribution is totally different.
- Simulations performed using the parameters obtained for the different sets revealed, that in the case of non-total oxygen conversion set the predominant surface specie is the water and for the total oxygen conversion set is the oxygen..
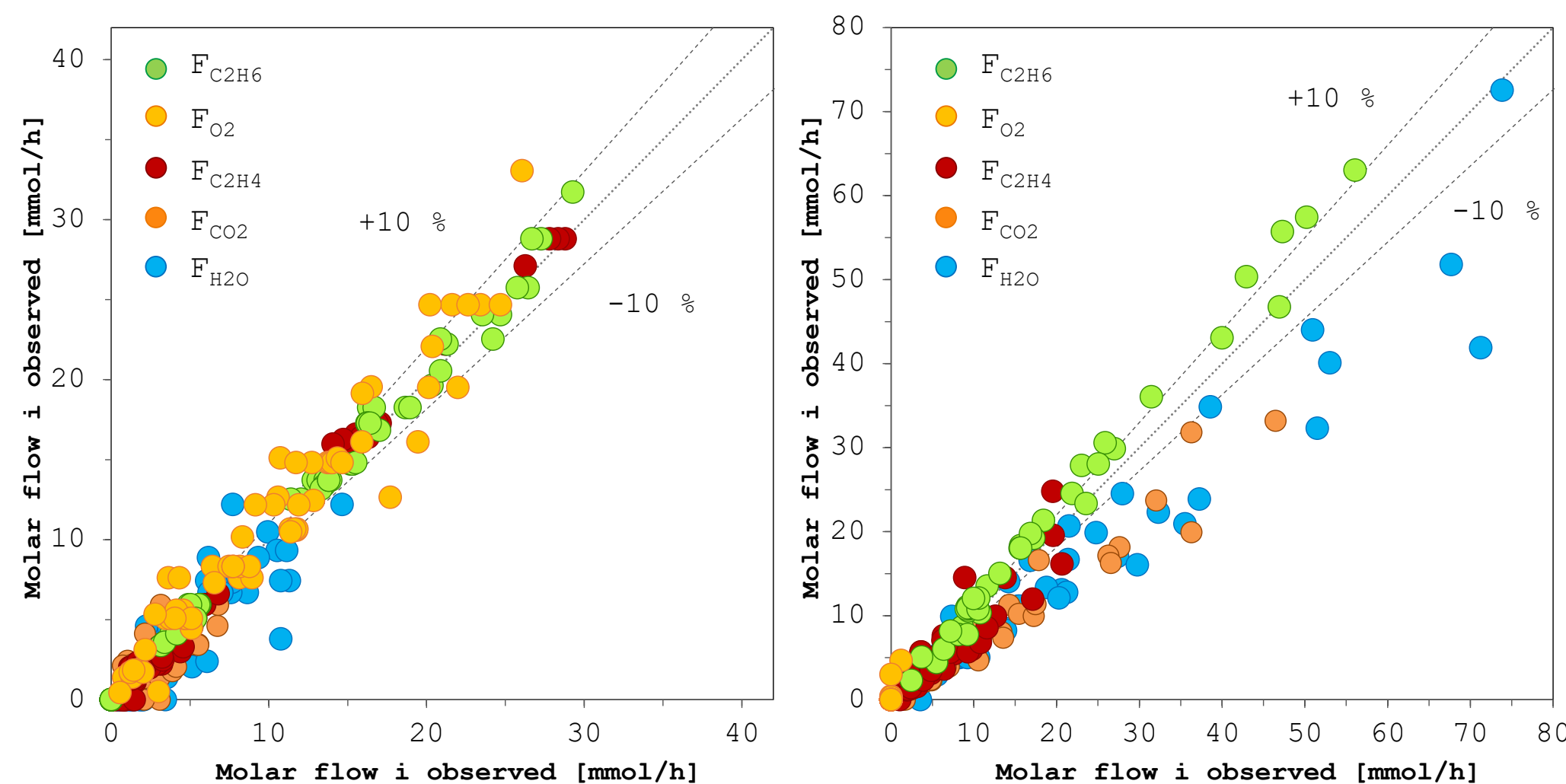
EXPERIMENTAL TEST RESULTS

Not-Total Oxygen conversion regime — **Total Oxygen conversion regime**

Legend: Oxygen conversion · Ethane conversion · Ethylene selectivity · CO$_2$ selectivity

(Conversion and selectivity [%] vs Temperature [°C])
(Conversion and selectivity [%] vs Dimensionless W/F$_{Ao}$ [%])

PARITY PLOTS

F$_{C2H6}$, F$_{O2}$, F$_{C2H4}$, F$_{CO2}$, F$_{H2O}$
Molar flow i observed [mmol/h]
+10 % / −10 %

LHHW MODEL

Reaction step	σ$_I$	σ$_{II}$	σ$_{III}$	Reaction rate expression
A O$_{2(g)}$ + 2* ⇌ 2 O*	1	7	3	$r_A = \vec{k}_A p_{O_2} N_T \theta_s^2 - \overleftarrow{k}_A N_T \theta_O^2$
B C$_2$H$_{6(g)}$ + * ⇌ C$_2$H$_6$*	2	2	0	$r_B = \vec{k}_B p_{C_2H_6} N_T \theta_s - \overleftarrow{k}_B N_T \theta_{C_2H_6}$
1 C$_2$H$_6$* + O* ⟶ C$_2$H$_4$* + H$_2$O*	2	0	0	$r_1 = k_1 N_T \theta_{C_2H_6} \theta_O$
2 C$_2$H$_6$* + O* ⟶ …$^{+6O^*}$ 2 CO$_2$* + 3 H$_2$O* + 3*	0	2	0	$r_2 = k_2 N_T \theta_{C_2H_6} \theta_O$
3 C$_2$H$_4$* + O* ⟶ …$^{+5O^*}$ 2 CO$_2$* + 2 H$_2$O* + 3*	0	0	1	$r_3 = k_3 N_T \theta_{C_2H_4} \theta_O$
C C$_2$H$_4$* ⇌ C$_2$H$_4$ (g) + *	2	0	1	$r_C = \vec{k}_C N_T \theta_{C_2H_4} - \overleftarrow{k}_C p_{C_2H_4} N_T \theta_s$
D CO$_2$* ⇌ CO$_2$ (g) + *	0	4	2	$r_D = \vec{k}_D N_T \theta_{CO_2} - \overleftarrow{k}_D p_{CO_2} N_T \theta_s$
E H$_2$O* ⇌ H$_2$O (g) + *	2	6	2	$r_E = \vec{k}_E N_T \theta_{H_2O} - \overleftarrow{k}_D p_{H_2O} N_T \theta_s$

ESTIMATED PARAMETERS

Not-Total Oxygen conversion regime PARAMETERS

	P-Factors		Activation Energies [kJ/mol]
A$_{-1}$	8.84 X 10^{+09}	EA$_{-1}$	85.67 ± 2.36
A$_{-2}$	3.20 X 10^{+10}	EA$_{-2}$	95.18 ± 1.89
A$_{-3}$	5.82 X 10^{+09}	EA$_{-3}$	101.43 ± 3.24
A$_{O2}$_F	1.76 X 10^{+02}	EA$_{O2}$_F	0.064 ± 0.002
A$_{O2}$_R	5.21 X 10^{+11}	EA$_{O2}$_R	66.88 ± 0.82
A$_{C2H6}$_F	1.87 X 10^{+02}	EA$_{C2H6}$_F	0.084 ± 0.0011
A$_{C2H6}$_R	1.49 X 10^{+13}	EA$_{C2H6}$_R	85.97 ± 0.90
AC$_{2H4}$_F	1.49 X 10^{+13}	EA$_{C2H4}$_F	99.63 ± 1.66
A$_{C2H4}$_R	2.01 X 10^{+02}	EA$_{C2H4}$_R	0.025 ± 0.002
A$_{CO2}$_F	1.49 X 10^{+13}	EA$_{CO2}$_F	87.31 ± 2.79
A$_{CO2}$_R	1.28 X 10^{+02}	EA$_{CO2}$_R	0.019 ± 0.001
A$_{H2O}$_F	1.49 X 10^{+13}	EA$_{H2O}$_F	104.2 ± 0.89
A$_{H2O}$_R	3.13 X 10^{+02}	EA$_{H2O}$_R	0.01 ± 0.002

Total Oxygen conversion regime PARAMETERS

	P-Factors		Activation Energies [kJ/mol]
A$_{-1}$	1.73 X 10^{+10}	EA$_{-1}$	87.63 ± 1.93
A$_{-2}$	5.30 X 10^{+10}	EA$_{-2}$	96.40 ± 4.66
A$_{-3}$	3.82 X 10^{+10}	EA$_{-3}$	119.09 ± 8.57
A$_{O2}$_F	1.76 X 10^{+02}	EA$_{O2}$_F	0.006 ± 4E-04
A$_{O2}$_R	5.21 X 10^{+11}	EA$_{O2}$_R	70.00 ± 3.79
A$_{C2H6}$_F	1.87 X 10^{+02}	EA$_{C2H6}$_F	0.007 ± 4E-4
A$_{C2H6}$_R	1.49 X 10^{+13}	EA$_{C2H6}$_R	71.32 ± 2.58
AC$_{2H4}$_F	1.49 X 10^{+13}	EA$_{C2H4}$_F	74.43 ± 3.77
A$_{C2H4}$_R	2.01 X 10^{+02}	EA$_{C2H4}$_R	0.01 ± 8E-4
A$_{CO2}$_F	1.49 X 10^{+13}	EA$_{CO2}$_F	71.44 ± 3.87
A$_{CO2}$_R	1.28 X 10^{+02}	EA$_{CO2}$_R	0.001 ± 6E-5
A$_{H2O}$_F	1.49 X 10^{+13}	EA$_{H2O}$_F	72.75 ± 2.58
A$_{H2O}$_R	3.13 X 10^{+02}	EA$_{H2O}$_R	0.001 ± 8E-5

COVERAGE SURFACE PREDICTIONS

Not-Total Oxygen conversion regime
(Coverage fraction of i, θ$_i$ vs Temperature [°C])
θ$_{H2O}$, θ$_{C2H6}$, θ$_{O2}$, θ$_{C2H4}$, θ$_{CO2}$

Total Oxygen conversion regime
(Coverage fraction of i, θ$_i$ vs Temperature [°C])
θ$_{H2O}$, θ$_{C2H6}$, θ$_{O2}$, θ$_{C2H4}$, θ$_{CO2}$
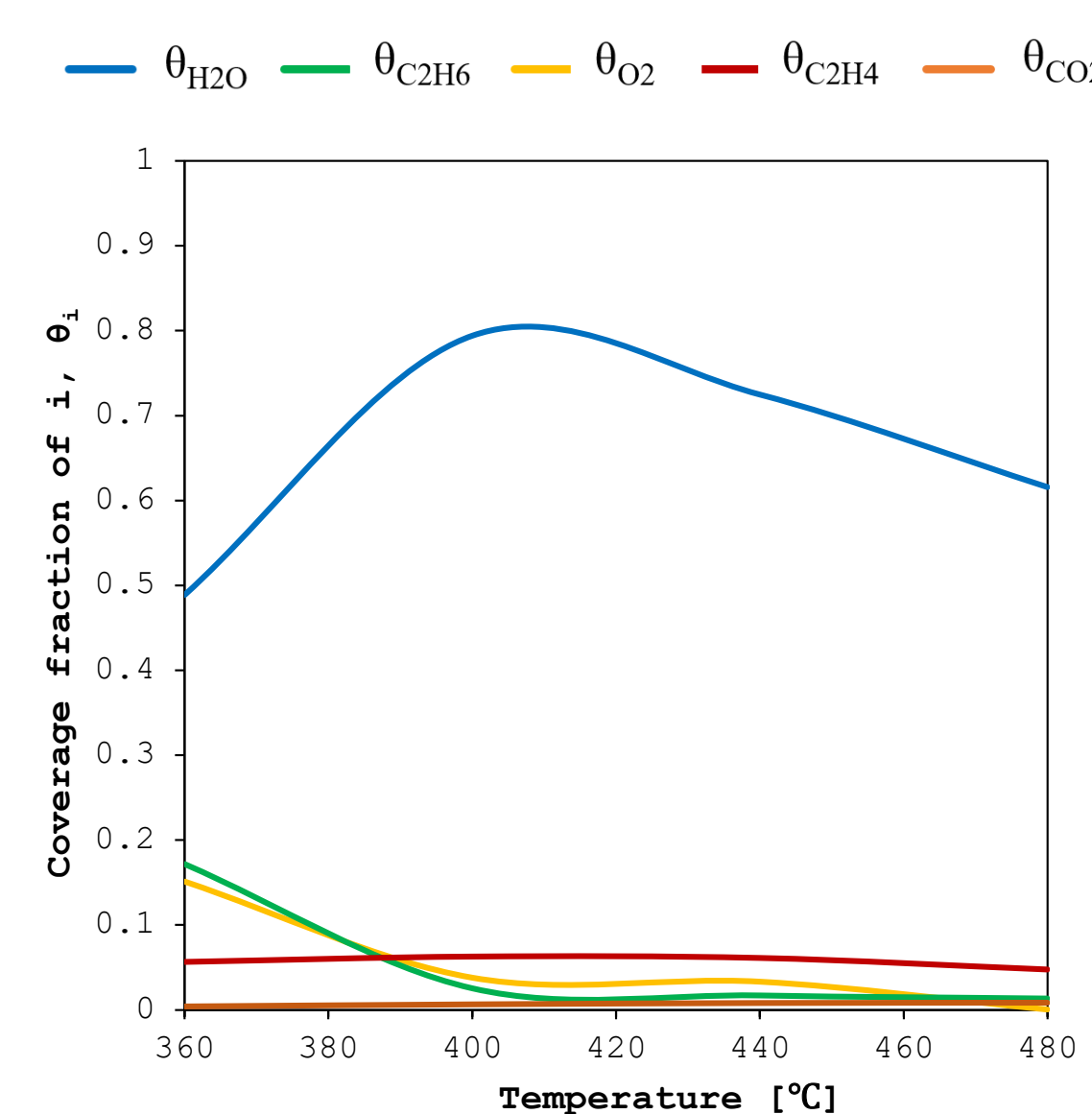
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CONCLUSIONS

A kinetic study of the ODH-C$_2$ was undertaken over a promising NiSnO catalyst, using experimental sets at non-total and total oxygen conversion under kinetic regime. Experimental results, demonstrated that oxygen conversions leads to different trends on the ethane conversion and selectivity to ethylene. Kinetic modeling proved that to develop studies under different oxygen regimes leads to obtained significant differences in the estimated parameters, which could affect future scale up of an industrial reactor.

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