SUPPORTING INFORMATION A

A.1. Mass transfer limitations

Catalytic propane dehydrogenation requires two diffusion steps: 1) to the catalyst surface (external diffusion); and 2) within the catalyst pores (internal diffusion). The measurement of the reaction kinetics is compromised if the rate of mass transfer is lower than that of the chemical step or there is not an effective heat transfer.[1,2] We checked the absence of external and internal mass transfer limitations following standard experimental criteria by increasing the overall volumetric flow rate (q) and decreasing the catalyst particle size (d) at constant (W/F_{A0}).[3,4] Figure A1 shows the results where X_{A0} reaches a plateau at $q \geq 80$ cm^3 min^{-1} and $d \leq 200$ μm. This is indicative of operation under chemical control.

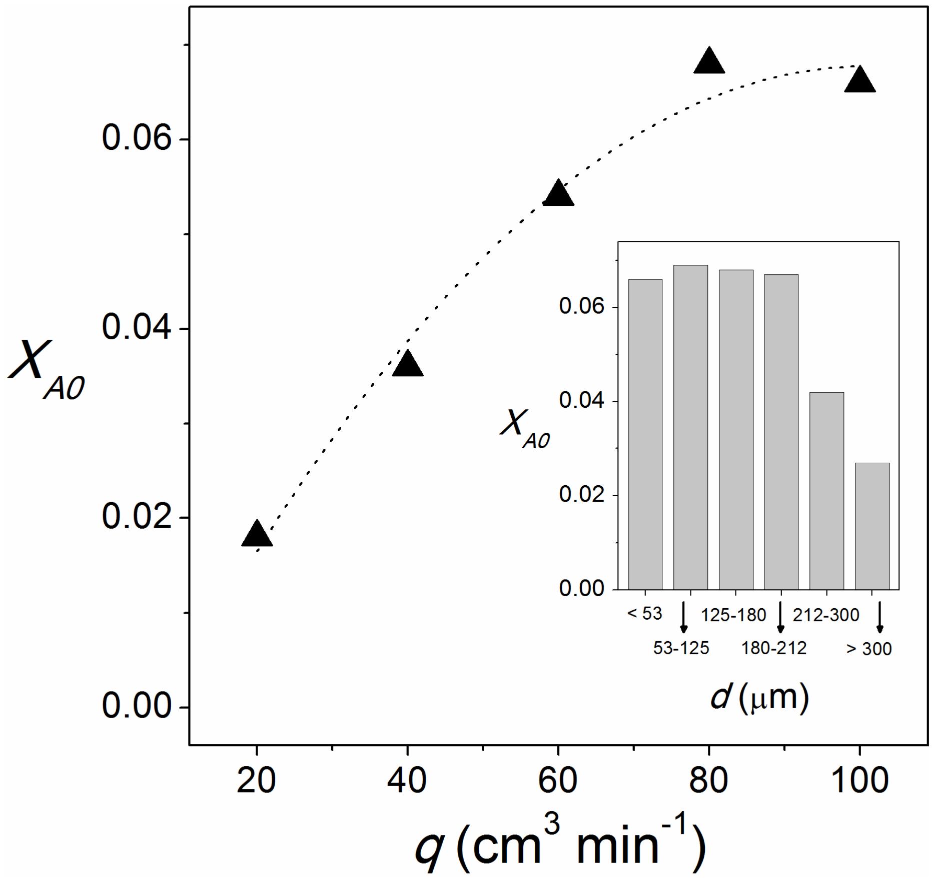

Figure A1: Variation of initial propane fractional conversion (X_{A0}) with the total inlet volumetric flow rate (q) for reaction over Pt-Sn/Al_2O_3 at d = 150 μm. Inset: variation of X_{A0} with the catalyst particle size (d) at q = 80 cm^3 min^{-1}. (W/F_{A0}) = 0.04 g h mol^{-1}

A.2. Heat transport limitations

This section presents all necessary steps and calculations in order to demonstrate that the reactions have been conducted in a regime free from heat transport limitations. Table A1 shows the reaction conditions (in terms of partial pressures/molar fractions and temperature) and the initial propane consumption rate for each experiment.

A.2.1. Estimation of the reacting fluid density (ρ_{mix}, kg m^{-3})

The density of the reacting fluid mixture is

$$\rho_{mix} = M_{mix} / \bar{V}_{mix} \tag{A1}$$

$$M_{mix} = \sum_{i=1}^{n} \left(y_i \times M_i \right) \tag{A2}$$

where M_{mix} and M_i are the average molecular weight of the fluid and compound i (g mol^{-1}) and y_i is the molar fraction of compound i. $\bar{V}_{mix}$ is the molar volume of the fluid:

$$\bar{V}_{mix} = \left(Z_{mix} \times R_g \times T \right) / P \tag{A3}$$

where P is the pressure (101330 N m^{-2}), T is the temperature (K) and R_g is the ideal gas constant (8.314 J mol^{-1} K^{-1}). Z_{mix} is the compressibility factor of the fluid:

$$Z_{mix} = Z_{mix}^{(0)} + \omega_{mix} \times Z_{mix}^{(1)} \tag{A4}$$

where ω_{mix} is the fluid acentric factor

$$\omega_{mix} = \sum_{i=1}^{n} \left(y_i \times \omega_i \right) \tag{A5}$$

ω_i is the acentric factor of compound i and $Z_{mix}^{(0)}$ and $Z_{mix}^{(1)}$ are acentric contributions to Z_{mix} which are found graphically using the fluid reduced temperature ($T_{r,mix}$) and pressure ($P_{r,mix}$)

$$T_{r,mix} = T / T_{c,mix} \tag{A6}$$

$$P_{r,mix} = P / P_{c,mix} \tag{A7}$$

The values of $T_{c,mix}$ (the fluid critical temperature, K) and $P_{c,mix}$ (the fluid critical pressure, N m^{-2}) are calculated from

$$T_{c,mix} = \sum_{i=1}^{n} \left(y_i \times T_{c,i} \right) \tag{A8}$$

$$P_{c,mix} = \frac{T_{c,mix} \times R_g \times \sum_{i=1}^{n} \left(y_i \times Z_{c,i} \right)}{\sum_{i=1}^{n} \left(y_i \times \bar{V}_{c,i} \right)} \tag{A9}$$

where $T_{c,i}$ is the critical temperature of compound i (K), $\bar{V}_{c,i}$ is the critical molar volume of compound i (m^3 mol^{-1}). $Z_{c,i}$ is the critical compressibility factor of compound i,

$$Z_{c,i} = \frac{\bar{V}_{c,i} \times P_{c,i}}{T_{c,i} \times R_g} \tag{A10}$$

where $P_{c,i}$ is the critical pressure of compound i (N m^{-2}). The critical constants ($T_{c,i}$, $P_{c,i}$ and $\bar{V}_{c,i}$) and acentric factors (ω_i) where taken from reference literature[5] or estimated by group contribution methods, as established elsewhere.[6] The values of ρ_{mix} at each experimental condition can be found in Table A2.

A.2.2. Estimation of the reacting fluid dynamic viscosity (μ_{mix}, kg m^{-1} s^{-1})

The dynamic viscosity of the reacting fluid mixture is

$$\mu_{mix} = \sum_{i=1}^{n} \left(\frac{y_i \times \mu_i}{\sum_{j=1}^{n} \left(y_j \times \phi_{ij} \right)} \right) \tag{A11}$$

where ϕ_{ij} is an interaction parameter

$$\phi_{ij} = \frac{\left(1 + \left(\mu_i / \mu_j \right)^{1/2} \times \left(M_j / M_i \right)^{1/4} \right)^2}{\left(8 \times \left(1 + M_i / M_j \right) \right)^{1/2}} \tag{A12}$$

$$\phi_{ji} = \phi_{ij} \times \left(M_i / M_j \right) \times \left(\mu_j / \mu_i \right) \tag{A13}$$

and μ_i is the dynamic viscosity of compound i (kg m^{-1} s^{-1}). The latter was found graphically[6] (in cP) for each compound at different temperatures (573 K–823 K) and fitted to

$$\mu_{Propane} = \left(2.40 \times 10^{-5} \right) \times T + \left(1.35 \times 10^{-3} \right) \tag{A14}$$

$$\mu_{Propene} = \left(2.82 \times 10^{-5} \right) \times T + \left(0.48 \times 10^{-3} \right) \tag{A15}$$

$$\mu_{H_2} = \left(1.34 \times 10^{-5} \right) \times T + \left(6.20 \times 10^{-3} \right) \tag{A16}$$

$$\mu_{Ar} = \left(5.23\times10^{-5}\right)\times T + \left(8.23\times10^{-3}\right) \tag{A17}$$

The values of μ_{mix} at each experimental condition can be found in Table A2.

A.2.3. Estimation of the reacting fluid heat capacity ($C_{p,mix}$, J K^{-1} mol^{-1})

The heat capacity of the reacting fluid mixture is

$$C_{p,mix} = \sum_{i=1}^{n}\left(y_i \times C_{p,i}\right) \tag{A18}$$

$$C_{p,i} = A + B\times T + C\times T^2 + D\times T^3 + E\times T^4 \tag{A19}$$

where $C_{p,i}$ are the heat capacities of compound i (J K^{-1} mol^{-1}) and the constants (A–E) were found elsewhere[5] (range of validity: 50 K–1000 K) and are listed in Table A3. Table A2 presents the values of $C_{p,mix}$ at each experimental conditions.

A.2.4. Estimation of the reacting fluid thermal conductivity (λ_{mix}, J K^{-1} m^{-1} s^{-1})

The thermal conductivity of the reacting fluid mixture is

$$\lambda_{mix} = \sum_{i=1}^{n}\left(\frac{y_i \times \lambda_i}{\sum_{j=1}^{n}\left(y_i \times A_{ij}\right)}\right) \tag{A20}$$

where λ_i is the thermal conductivity of compound i (J K^{-1} m^{-1} s^{-1}) and A_{ij} is an interaction parameter

$$A_{ij} = \frac{\left(1+\left(g_i/g_j\right)^{1/2}\times\left(M_j/M_i\right)^{1/4}\right)^2}{\left(8\times\left(1+M_i/M_j\right)\right)^{1/2}} \tag{A21}$$

$$\frac{g_i}{g_j} = \left(\frac{f\left(T_{r,i}\right)}{f\left(T_{r,j}\right)}\right)\times\left(\frac{\Gamma_j}{\Gamma_i}\right) \tag{A22}$$

$$f\left(T_{r,i}\right) = \exp\left(0.0464\times T_{r,i}\right) - \exp\left(-0.2412\times T_{r,i}\right) \tag{A23}$$

$$\Gamma_i = \left(T_{c,i}\right)^{1/6}\times\left(P_{c,i}\right)^{-2/3}\times\left(M_i\right)^{1/2} \tag{A24}$$

The estimation of λ_i is dependent on the nature of the compound,[6] drawing on the method of Thodos for propane and propene (eqn. (A25)) and the averaged Eucken correction for H_2 and Ar (eqns. (A26–A28)).

$$\lambda_i = \frac{\left(14.52\times T_{r,i} - 5.14\right)^{3/2} \times C_{p,i} \times 10^{-6}}{\Gamma_i} \tag{A25}$$

$$\bar{\lambda}_i = \left(\lambda_{Eucken1} + \lambda_{Eucken2}\right)/2 \tag{A26}$$

$$\lambda_{Eucken1} = \left(\mu_i / M_i\right)\left[C_{p,i} - R_g + 4.47\right] \tag{A27}$$

$$\lambda_{Eucken2} = \left(\mu_i / M_i\right)\left[\left(C_{p,i} - R_g\right)\times 1.32 + 3.52\right] \tag{A28}$$

The values of λ_{mix} at each experimental condition can be found in Table A2.

A.2.5. Estimation of propane diffusivity in the reacting fluid ($D_{A,mix}$, $m^2\ s^{-1}$)

The diffusivity of propane in the reacting fluid mixture is

$$D_{A,mix} = \sum_{i=1}^{n}\left(\frac{1}{y_j / D_{A,j}}\right) \tag{A29}$$

where $D_{A,j}$ is the diffusivity of propane in component j and can be estimated from the Chapman-Enskog relationship (in $cm^2\ s^{-1}$)

$$D_{A,j} = \frac{0.00266\times T^{3/2}}{P\times M_{Aj}^{1/2} \times \sigma_{Aj}^{2} \times \Omega_D} \tag{A30}$$

$$M_{Aj} = \frac{2}{\left(1/M_A\right) - \left(1/M_j\right)} \tag{A31}$$

$$\sigma_{Aj} = \left(\sigma_A + \sigma_j\right)/2 \tag{A32}$$

The value of Ω_D, the diffusion collision integral, can be calculated from

$$\Omega_D = \frac{1.06036}{\left(T^*\right)^{0.1561}} + \frac{0.193}{\exp\left(0.47635\times T^*\right)} + \frac{1.03587}{\exp\left(1.52996\times T^*\right)} + \frac{1.76474}{\exp\left(3.89411\times T^*\right)} \tag{A33}$$

$$T^* = T\times\left(k/\varepsilon\right)_{Aj} \tag{A34}$$

$$\left(k/\varepsilon\right)_{Aj} = \left[\left(k/\varepsilon\right)_A \times \left(k/\varepsilon\right)_j\right]^{1/2} \tag{A35}$$

Data for σ_i (Å) and $(\varepsilon/k)_i$ (K) can be found in the literature[5] and Table A2 presents the values of $D_{A,mix}$ for each experimental point.

A.2.6. Estimation of the fluid-to-catalyst heat transfer coefficient (h, $J\ K^{-1}\ m^{-2}\ s^{-1}$)

The fluid-to-catalyst heat transfer coefficient is calculated from

$$\left(\frac{h\times d_p}{\lambda_{mix}}\right)=\left(\frac{0.428}{\varepsilon_b}\right)\times \mathrm{Re}^{0.641}\times \mathrm{Pr}^{1/3} \quad 3<\mathrm{Re}<2000$$
$$\left(\frac{h\times d_p}{\lambda_{mix}}\right)=0.07\times \mathrm{Re} \quad 0.1<\mathrm{Re}<10 \qquad \text{(A36)}$$

where d_p is the catalyst particle size (150 μm), ε_b is the bed porosity (*ca*. 0.5 based on Hg and He porosimetry measurements). Re and Pr are the Reynolds and Prandtl dimensionless numbers and estimated as

$$\mathrm{Re}=\frac{u_{mix}\times d_p\times \rho_{mix}}{\mu_{mix}} \qquad \text{(A37)}$$

$$\mathrm{Pr}=\frac{\mu_{mix}\times C_{p,mix}}{\lambda_{mix}} \qquad \text{(A38)}$$

where the velocity u_{mix} is 0.11 m s^{-1} (*i.e*. 80 cm^3 min^{-1} of reacting fluid flowing through a 4 mm *i.d*. reactor). The values of h for each experiment are gathered in Table A4

A.2.7. Estimation of the propane mass transfer coefficient (k_f, m s^{-1})

The propane mass transfer coefficient is calculated from

$$\left(\frac{k_f\times d_p}{D_{A,mix}}\right)=\left(\frac{0.357}{\varepsilon_b}\right)\times \mathrm{Re}^{0.641}\times \mathrm{Sc}^{1/3} \quad 3<\mathrm{Re}<2000$$
$$\left(\frac{k_f\times d_p}{D_{A,mix}}\right)=0.07\times \mathrm{Re} \quad 0.1<\mathrm{Re}<10 \qquad \text{(A39)}$$

where the Schmidt number (Sc) can be estimated as

$$\mathrm{Sc}=\frac{\mu_{mix}}{\rho_{mix}\times D_{A,mix}} \qquad \text{(A40)}$$

The values of k_f for each experiment are given in Table A4.

A.2.8. External heat transfer criterion

The criterion for external heat transfer limitations is

$$\left(\frac{Ea}{R_g\times T}\right)\times\left(\frac{\left\|\Delta\bar{H}\right\|\times k_f\times C_b}{h\times T}\right)\times\left(\frac{r_0'}{a\times k_f\times C_b}\right)<0.05 \qquad \text{(A41)}$$

$$\Delta\bar{H}=\left(6.97\times10^{-9}\right)\times T^3+\left(-2.69\times10^{-5}\right)\times T^2+\left(3.25\times10^{-2}\right)\times T+116.78 \quad \text{(A42)}$$

$$C_b = \frac{P_A}{R_g \times T} \tag{A43}$$

where (Ea/R_g) is 1593 K, $\Delta \bar{H}$ is the specific reaction enthalpy (kJ mol^{-1}, eqn. (A42)), C_b is the concentration of propane in the reacting fluid (mol m^{-3}, eqn. (A43)) and a = $6/d_p$. r_0' is the propane consumption rate (mol s^{-1} m^{-3})

$$r_0' = r_0 \times \rho_{\text{Skeletal}} \tag{A44}$$

where r_0 is the propane consumption rate in mol s^{-1} kg^{-1} and ρ_{Skeletal} = 1606 kg m^{-3}, as estimated from He porosimetry. The results presented in Table A4 demonstrate that the reactions were run in absence of external heat transport limitations at all conditions during the study.

A.2.9. Internal heat transfer criterion

The criterion for internal heat transfer limitations is

$$\left(\frac{Ea}{R_g \times T}\right) \times \left(\frac{\left\|\Delta \bar{H}\right\| \times D_{A,mix} \times C_s}{\lambda_{Catalyst} \times T}\right) \times \left(\frac{r_0' \times L^2}{D_{A,mix} \times C_s}\right) < 0.1 \tag{A45}$$

where $\lambda_{Catalyst}$ is the effective thermal conductivity of the catalyst (J K^{-1} m^{-1} s^{-1}), taken as equal to that from the γ-Al_2O_3 support and drawing from reference literature[5]

$$\lambda_{Catalyst} = 16896 \times T^{-1.0793} \tag{A46}$$

C_s is the concentration of propane at the catalyst surface (which is taken as equal to C_b for absence of limitations) and L = $d_p/6$. The results presented in Table A4 demonstrate that the reactions were run in absence of internal heat transport limitations at all conditions during the study.

References

[1] S. Gómez-Quero, F. Cárdenas-Lizana, M. A. Keane, *AIChE J.* **2009**, *56*, 756.

[2] G. F. Froment, K. B. Bischoff, J. de Wilde, *Chemical Reactor Analysis and Design*, John Wiley & Sons., Hoboken, **2011**.

[3] L. Forni, *Catal. Today* **1997**, *34*, 353.

[4] C. Perego, S. Peratello, *Catal. Today* **1999**, *52*, 133.

[5] B. E. Poling, J. M. Prausnitz, J. P. O'connell, *The Properties of Gases and Liquids*, McGraw-Hill, New York, **2001**.

[6] R. H. Perry, D. W. Green, *Perry's Chemical Engineering' Handbook*, McGraw-Hill, New York, **1973**.

Table A1: Experimental conditions (in terms of partial pressure of compound *i* and temperature) and initial propane consumption rate.

Experiment	P_{A0} (atm)	P_{E0} (atm)	P_{H0} (atm)	P_{R0} (atm)	T (K)	r_0 (mol^{-1} g^{-1} h^{-1})
1	0.125	0	0	0.875		0.595
2	0.250	0	0	0.750		1.268
3	0.375	0	0	0.625		1.522
4	0.500	0	0	0.500		1.812
5	0.625	0	0	0.375		2.086
6	0.750	0	0	0.250		2.282
7	0.875	0	0	0.125		2.749
8	0.125	0.125	0	0.750		0.522
9	0.125	0.250	0	0.625		0.460
10	0.125	0.375	0	0.500		0.405
11	0.125	0.500	0	0.375	723	0.325
12	0.125	0.625	0	0.250		0.292
13	0.125	0.750	0	0.125		0.275
14	0.125	0.875	0	0		0.166
15	0.125	0	0.125	0.750		0.503
16	0.125	0	0.250	0.625		0.479
17	0.125	0	0.375	0.500		0.540
18	0.125	0	0.50	0.375		0.559
19	0.125	0	0.625	0.250		0.650
20	0.125	0	0.750	0.125		0.632
21	0.125	0	0.875	0		0.828
22	0.0625	0	0	0.9375		0.620
23	0.125	0	0	0.875		1.271
24	0.1875	0	0	0.8125		1.677
25	0.250	0	0	0.750		2.068
26	0.3125	0	0	0.6875		2.172
27	0.375	0	0	0.625		2.295
28	0.500	0	0	0.500		2.450
29	0.625	0	0	0.375		2.822
30	0.750	0	0	0.250		2.990
31	0.875	0	0	0.125		3.251
32	0.125	0.125	0	0.750		1.214
33	0.125	0.250	0	0.625		0.979
34	0.125	0.300	0	0.575	823	0.776
35	0.125	0.375	0	0.500		0.598
36	0.125	0.500	0	0.375		0.552
37	0.125	0.625	0	0.250		0.385
38	0.125	0.750	0	0.125		0.417
39	0.125	0.875	0	0		0.287
40	0.125	0	0.125	0.750		1.126
41	0.125	0	0.250	0.625		1.092
42	0.125	0	0.375	0.500		1.136
43	0.125	0	0.50	0.375		1.246
44	0.125	0	0.625	0.250		1.311
45	0.125	0	0.750	0.125		1.338
46	0.125	0	0.875	0		1.467

Table A2: Physico-chemical properties of the reacting fluid at the stated reaction conditions (see Table 2).

Experiment	ρ_{mix} (kg m^{-3})	$\mu_{mix}\times10^5$ (kg m^{-1} s^{-1})	$C_{p,mix}$ (J K^{-1} mol^{-1})	λ_{mix} (J K^{-1} m^{-1} s^{-1})	$D_{A,mix}\times10^4$ (m^2 s^{-1})
1	0.68	3.99	36.4	0.043	0.57
2	0.69	3.50	52.1	0.050	0.67
3	0.70	3.10	67.7	0.056	0.80
4	0.71	2.76	83.4	0.062	1.01
5	0.72	2.48	99.0	0.067	1.34
6	0.72	2.25	114.7	0.072	2.01
7	0.73	2.05	130.3	0.077	4.02
8	0.69	3.58	49.1	0.051	0.54
9	0.69	3.22	61.7	0.058	0.50
10	0.69	2.92	74.4	0.064	0.47
11	0.70	2.66	87.0	0.070	0.45
12	0.70	2.43	99.7	0.076	0.42
13	0.71	2.23	112.3	0.081	0.40
14	0.71	2.05	125.0	0.086	0.38
15	0.60	3.90	37.5	0.045	0.64
16	0.52	3.77	38.6	0.048	0.73
17	0.44	3.58	39.7	0.052	0.85
18	0.36	3.29	40.8	0.057	1.01
19	0.28	2.84	41.9	0.065	1.25
20	0.20	2.11	42.9	0.079	1.63
21	0.12	0.77	44.0	0.102	2.36
22	0.60	4.77	29.3	0.045	0.67
23	0.60	4.45	37.8	0.050	0.72
24	0.60	4.17	46.4	0.054	0.77
25	0.61	3.91	54.9	0.058	0.84
26	0.61	3.68	63.4	0.063	0.91
27	0.61	3.47	71.9	0.066	1.00
28	0.62	3.10	89.0	0.074	1.25
29	0.63	2.79	106.1	0.080	1.67
30	0.64	2.53	123.1	0.086	2.51
31	0.64	2.30	140.2	0.092	5.01
32	0.60	4.00	51.6	0.059	0.67
33	0.61	3.62	65.4	0.068	0.63
34	0.61	3.48	70.9	0.071	0.62
35	0.61	3.29	79.1	0.076	0.59
36	0.61	3.00	92.9	0.083	0.56
37	0.62	2.74	106.7	0.090	0.53
38	0.62	2.52	120.4	0.097	0.51
39	0.63	2.32	134.2	0.103	0.48
40	0.53	4.35	38.9	0.053	0.80
41	0.46	4.20	40.1	0.057	0.91
42	0.39	3.98	41.2	0.062	1.06
43	0.32	3.66	42.3	0.069	1.26
44	0.25	3.16	43.4	0.078	1.56
45	0.18	2.34	44.5	0.092	2.04
46	0.11	0.84	45.6	0.115	2.94

Table A3: Parameters for the calculation of $C_{p,i}$ in eqn. (A19).

Parameter	**Propane**	**Propene**	**H_2**	**Ar**
A	3.847	3.834	2.883	2.5
$B\times10^3$	5.131	3.893	3.681	0
$C\times10^5$	6.011	4.688	-0.772	0
$D\times10^8$	-7.893	-6.013	0.692	0
$E\times10^{11}$	3.079	2.283	-0.213	0

Table A4: Heat transfer (h) and mass transfer (k_f) coefficients and application of critera for the presence of limitations at the stated reaction conditions.

Experiment	h ($\mathrm{J\ K^{-1}\ m^{-2}\ s^{-1}}$)	k_f ($\mathrm{m\ s^{-1}}$)	*External Criterion* $\times 10^4$	*Internal Criterion* $\times 10^8$
1	5.5	0.007	4.8	0.5
2	7.3	0.010	7.6	1.0
3	9.4	0.013	7.1	1.2
4	11.7	0.019	6.8	1.4
5	14.4	0.029	6.4	1.6
6	17.2	0.048	5.8	1.8
7	20.4	0.107	5.9	2.2
8	7.2	0.008	3.2	0.4
9	9.2	0.008	2.2	0.4
10	11.3	0.008	1.6	0.3
11	13.7	0.009	1.0	0.3
12	16.3	0.009	0.8	0.2
13	19.2	0.010	0.6	0.2
14	22.2	0.010	0.3	0.1
15	5.2	0.007	4.3	0.4
16	4.9	0.008	4.3	0.4
17	4.8	0.008	5.0	0.4
18	4.7	0.008	5.2	0.4
19	4.8	0.009	5.9	0.5
20	5.6	0.012	5.0	0.5
21	12.0	0.028	3.0	0.7
22	4.2	0.006	5.0	0.4
23	5.0	0.007	8.7	0.9
24	5.8	0.008	9.8	1.2
25	6.7	0.010	10.4	1.5
26	7.7	0.011	9.6	1.5
27	8.7	0.013	8.9	1.6
28	11.0	0.019	7.6	1.7
29	13.4	0.028	7.1	2.0
30	16.1	0.047	6.3	2.1
31	19.0	0.104	5.8	2.3
32	6.6	0.007	6.2	0.9
33	8.4	0.008	3.9	0.7
34	9.2	0.008	2.9	0.5
35	10.4	0.008	1.9	0.4
36	12.7	0.009	1.5	0.4
37	15.1	0.009	0.9	0.3
38	17.7	0.009	0.8	0.3
39	20.5	0.010	0.5	0.2
40	4.8	0.007	8.0	0.8
41	4.6	0.007	8.0	0.8
42	4.5	0.008	8.6	0.8
43	4.4	0.008	9.5	0.9
44	4.6	0.009	9.7	0.9
45	5.2	0.011	8.7	0.9
46	10.8	0.028	4.6	1.0

APPENDIX B

Perego and Peratello described the importance of thermodynamics in that the heat of reaction and maximum conversion determine the limits of the system.[1] We have accordingly analysed the thermodynamics of our case drawing on reference data for propane, propylene and hydrogen as a function of temperature.[2] The specific enthalpy ($\Delta\bar{H}$) as is given in eqn. (B1). The dehydrogenation of propane is strongly endothermic (≈129 kJ mol^{-1}) within 723 and 823 K.

$$\Delta\bar{H} = \left(6.97\times10^{-9}\right)\times T^3 + \left(-2.69\times10^{-5}\right)\times T^2 + \left(3.25\times10^{-2}\right)\times T + 116.78 \qquad \text{(B1)}$$

Similarly, the specific Gibbs free energy ($\Delta\bar{G}$, kJ mol^{-1}) and equilibrium constant (K_p, atm) are given in eqns. (B2) and (B3),

$$\Delta\bar{G} = \left(-0.137\right)\times T + 128.102 \qquad \text{(B2)}$$

$$K_p = \left(1.48\times10^{7}\right)\times \exp\left(-15403/T\right) \qquad \text{(B3)}$$

The equilibrium conversion was finally calculated using eqn. (B4)

$$\text{Equilibrium Conversion} = \sqrt{1/\left(1+P/K_p\right)} \qquad \text{(B4)}$$

Figure B1 presents the results. The maximum achievable fractional conversion in the temperature range studied (723 K ≤ T ≤ 823 K) lies between 0.09 and 0.32. These results are consistent with the works of Michorczyk *et al.*[3,4] and Assabumrungrat and co-workers.[5] Moreover, Weckhuysen and Schoonheydt reported that temperatures as high as 870 K are needed to achieve a 50% conversion.[6] Additionally, we studied the effect of the presence of propene and hydrogen (*i.e.* the reaction products, eqn. (B5)) in the composition of the inlet by using

$$a\,C_3H_8 \leftrightarrow b\,C_3H_6 + c\,H_2 \qquad \text{(B5)}$$

where a, b and c are the stoichiometric coefficients and the equilibrium fractional conversion is now calculated from eqns. (B6) and (B7).

$$\left[\left(P/K_p\right)+1\right]\times s^2 + \left[\left(P/K_p\right)\times\left(b+c\right)-\left(a-d\right)\right]\times s + \left[\left(P/K_p\right)\times\left(b\times c\right)-a\times d\right] = 0 \qquad \text{(B6)}$$

$$\text{Equilibrium Conversion} = \frac{a-s}{a} \qquad \text{(B7)}$$

Figure B2 shows the change in propane conversion with the propylene-to-propane (b/a) and hydrogen-to-propane (c/a) molar ratios. A unique surface is determined for each reaction temperature. At 700 K, the presence of propylene or hydrogen with propane decreases conversion, which falls to zero whenever b/a and c/a > 1. An increase in temperature (to 900 K) favours dehydrogenation where ratios *b*/*a* or *c*/*a* > 10 are needed to significantly decrease conversion at 900 K. This is an important outcome since in a typical industrial dehydrogenation operational mode, hydrogen is normally co-fed with propane as a means to supress coke formation.[7] The simultaneous presence of propylene and hydrogen have dramatic consequences where no conversion is observed whenever *b*/*a* and *c*/*a* > 5. Our results demonstrate the great impact of the presence of reaction products in the inlet stream, and the importance of this analysis for this reaction.

References:

[1] C. Perego, S. Peratello, *Catal. Today* **1999**, *52*, 133.

[2] D. R. Stull, E. F. Westburn., G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, John Wiley & Sons, Inc., New York, **1969**.

[3] P. Michorczyk, J. Ogonowski, *React. Kinet. Catal. Lett.* **2003**, *78*, 41.

[4] P. Michorczyk, J. Ogonowski, *Appl. Catal. A: General* **2003**, *251*, 425.

[5] S. Assabumrungrat, W. Jhoraleecharnchai., P. Praserthdam, S. Goto, *J. Chem. Eng. Jpn.* **2000**, *33*, 529.

[6] B. M. Weckhuysen, R. A. Schoonheydt, *Catal. Today* **1999**, *51*, 223.

[7] M. S. Voronetskii, L. P. Didenko, V. I. Savchenko, *Russ. J. Phys. Chem. B* **2009**, *3*, 216.

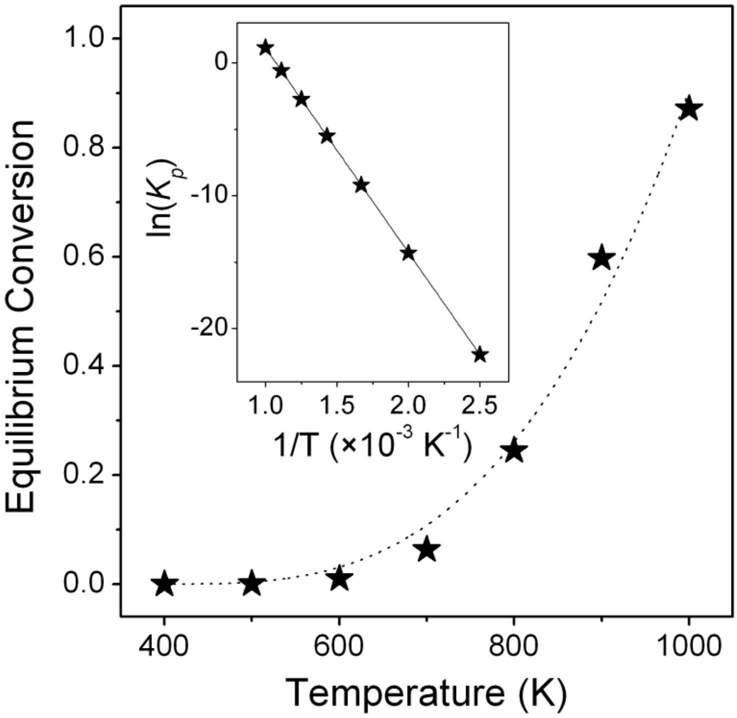

Figure B1: Propane dehydrogenation equilibrium conversion and constant (K_p, inset) as a function of temperature (see eqns. (B.3) and (B.4)).

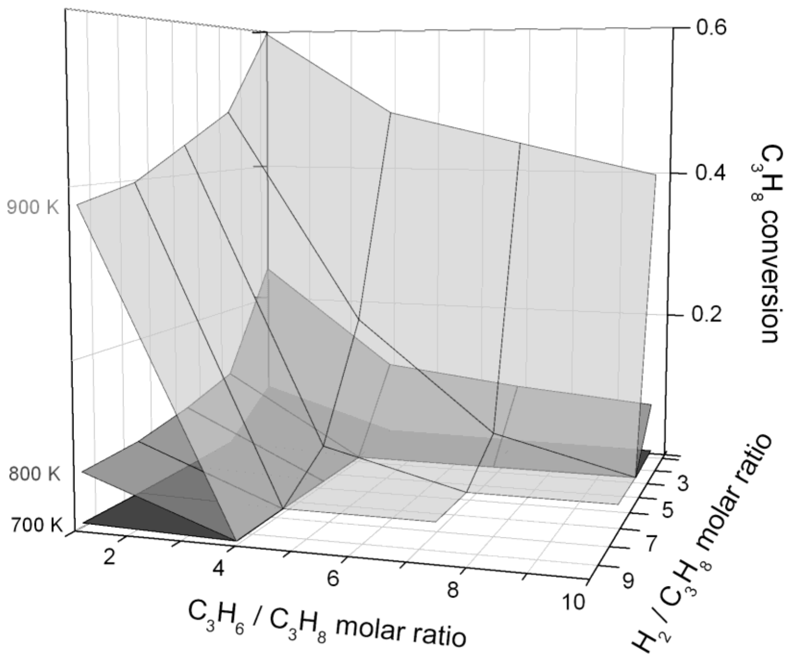

Figure B2: Propane dehydrogenation equilibrium conversion (Z-Axis) as a function of the ratios propylene/propane (X-Axis, left-to-right) and hydrogen/propane (Y-Axis, front-to-back). Each surface represents data calculated at different temperatures (see eqns. (B.6) and (B.7)).

APPENDIX C

The following document describes the step-by-step methodology taken to derive the mathematical expressions associated with the mechanistic models 5. Model III is taken here as representative example and it is based on three steps:

(i) Non-dissociative adsorption of propane (step 2).

(ii) Dehydrogenates to propylene (which remains adsorbed on the catalyst surface) releasing molecular hydrogen (step 4).

(iii) Propylene desorption (step 9).

This system can be represented by three reversible processes:

$$\mathrm{C_3H_8 + L \leftrightarrow C_3H_8 - L} \tag{C1}$$

$$\mathrm{C_3H_8 - L \leftrightarrow C_3H_6 - L + H_2} \tag{C2}$$

$$\mathrm{C_3H_6 - L \leftrightarrow C_3H_6 + L} \tag{C3}$$

Because these are considered elementary processes, the following rate expressions can be postulated:

$$r_2 = k_2 \times P_A \times C_L - k_{-2} \times C_{AL} \tag{C4}$$

$$r_2 = k_2 \left[P_A \times C_L - C_{AL} / K_2 \right] \tag{C5}$$

$$r_4 = k_4 \times C_{AL} - k_{-4} \times P_H \times C_{EL} \tag{C6}$$

$$r_4 = k_4 \times \left[C_{AL} - \left(P_H \times C_{EL} \right) / K_4 \right] \tag{C7}$$

$$r_9 = k_9 \times C_{EL} - k_{-9} \times P_E \times C_L \tag{C8}$$

$$r_9 = k_9 \times \left[C_{EL} - \left(P_E \times C_L \right) / K_{9,Desorption} \right] \tag{C9}$$

$$K_{eq} = \frac{P_E \times P_H}{P_A} = K_2 \times K_4 \times K_{9,Desorption} = \frac{K_2 \times K_4}{K_9} \tag{C10}$$

In these expressions, r_j is the rate of step j (mol g^{-1} h^{-1}), C_i is the concentration of species i (mol g^{-1}), P_i is the partial pressure of species i (atm), k_j is the kinetic constant of step j (k_2 in atm^{-1} min^{-1}, k_4 and k_9 in min^{-1}), K_j is the equilibrium constant of step j: K_2 (unitless) and K_4 (atm) stand for adsorption and $K_{9,Desorption}$ (= $1/K_9$, atm) for desorption. A = propane, E = propene, H = molecular hydrogen (H_2), L = free active centre, AL = active centre occupied by adsorbed propane, EL = active centre occupied by adsorbed propene. The balance with regard to the total number of active centres (T) is

$$C_T = C_L + C_{AL} + C_{EL} \tag{C11}$$

C.1. Rate limiting propane adsorption (step 2)

When propane adsorption is the slowest step, the following condition applies:

$$k_2 <<<< k_4, k_9 \tag{C12}$$

$$r_4/k_4 \to 0,\ r_9/k_9 \to 0 \tag{C13}$$

In this case, it is possible to express C_{EL} from eqn. (C9) in C_L

$$C_{EL} = K_9 \times C_L \times P_E \tag{C14}$$

Similarly for C_{AL} from eqns. (C7) and (C14)

$$C_{AL} = \left(K_9/K_4\right)\times C_L \times P_E \times P_H = \left(K_2/K_{eq}\right)\times C_L \times P_E \times P_H \tag{C15}$$

The site balance reads then

$$C_T = C_L + C_L \times P_E \times P_H \times \left(K_2/K_{eq}\right) + C_L \times P_E \times K_9 \tag{C16}$$

$$C_L = \frac{C_T}{\left[1 + P_E \times P_H \times \left(K_2/K_{eq}\right) + P_E \times K_9\right]} \tag{C17}$$

Substituting (C14, C15 and C17) in (C5), we have

$$r_2 = k_2\left[P_A \times C_L - C_L \times \left(K_2/K_{eq}\right)\times P_E \times P_H / K_2\right] \tag{C18}$$

$$r_2 = k_2 \times C_L\left[P_A - P_E \times P_H / K_{eq}\right] \tag{C19}$$

$$r_2 = \frac{k_2 \times C_T \times \left[P_A - P_E \times P_H / K_{eq}\right]}{\left[1 + P_E \times P_H \times \left(K_2/K_{eq}\right) + P_E \times K_9\right]} \tag{C20}$$

C.2. Rate limiting surface reaction (step 4)

When the surface reaction is the slowest step, the following condition applies:

$$k_4 <<<< k_2, k_9 \tag{C21}$$

$$r_2/k_2 \to 0,\ r_9/k_9 \to 0 \tag{C22}$$

In this case, it is possible to calculate C_{AL} from eqn. (C5) and C_{EL} from (C9)

$$C_{AL} = K_2 \times C_L \times P_A \tag{C23}$$

$$C_{EL} = K_9 \times C_L \times P_E \tag{C24}$$

The site balance is then

$$C_T = C_L + C_L \times P_A \times K_2 + C_L \times P_E \times K_9 \tag{C25}$$

$$C_L = \frac{C_T}{\left[1 + P_A \times K_2 + P_E \times K_9\right]} \tag{C26}$$

Substituting (C23, C24 and C26) in (C7), we have

$$r_4 = k_4 \times \left[K_2 \times C_L \times P_A - \left(P_H \times K_9 \times C_L \times P_E \right) / K_4 \right] \tag{C27}$$

$$r_4 = k_4 \times C_L \left[P_A - \left(P_H \times P_E \right) / \left(K_4 \times K_2 \times K_{9,Desorption} \right) \right] \tag{C28}$$

$$r_4 = \frac{k_4 \times K_2 \times C_T \times \left[P_A - P_E \times P_H / K_{eq} \right]}{\left[1 + P_A \times K_2 + P_E \times K_9 \right]} \tag{C29}$$

C.3. Rate limiting propene desorption (step 9)

When propene desorption is the slowest step, the following condition applies:

$$k_9 <<<< k_2, k_4 \tag{C30}$$

$$r_2 / k_2 \to 0, \; r_4 / k_4 \to 0 \tag{C31}$$

In this case, it is possible to calculate C_{AL} from eqn. (C5)

$$C_{AL} = K_2 \times C_L \times P_A \tag{C32}$$

Calculation of C_{EL} is possible from eqns. (C7) and (C32)

$$C_{EL} = \frac{K_4 \times C_{AL}}{P_H} = \frac{K_4 \times K_2 \times C_L \times P_A}{P_H} \tag{C33}$$

$$C_{EL} = C_L \times \left(K_{eq} / K_{9,Desorption} \right) \times \left(P_A / P_H \right) \tag{C34}$$

The site balance is then

$$C_T = C_L + C_L \times P_A \times K_2 + C_L \times \left(K_{eq} / K_{9,Desorption} \right) \times \left(P_A / P_H \right) \tag{C35}$$

$$C_L = \frac{C_T}{\left[1 + P_A \times K_2 + \left(K_{eq} / K_{9,Desorption} \right) \times \left(P_A / P_H \right) \right]} \tag{C36}$$

Substituting (C32, C34 and C36) in (C9), we have

$$r_9 = k_9 \times \left[C_L \times \left(K_{eq} / K_{9,Desorption} \right) \times \left(P_A / P_H \right) - \left(P_E \times C_L \right) / K_{9,Desorption} \right] \tag{C37}$$

$$r_9 = k_9 \times C_L \left[\left(K_9 \times K_{eq} \right) \times \left(P_A / P_H \right) - P_E \times K_9 \right] \tag{C38}$$

$$r_9 = k_9 \times C_L \times \left(\frac{K_{eq} \times K_9}{P_H} \right) \times \left[P_A - P_E \times P_H / K_{eq} \right] \tag{C39}$$

$$r_9 = \frac{k_9 \times K_{eq} \times K_9 \times C_T \times \left[P_A - P_E \times P_H / K_{eq} \right]}{\left[P_H + P_A \times P_H \times K_2 + \left(K_9 \times K_{eq} \right) \times P_A \right]} \tag{C40}$$