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.
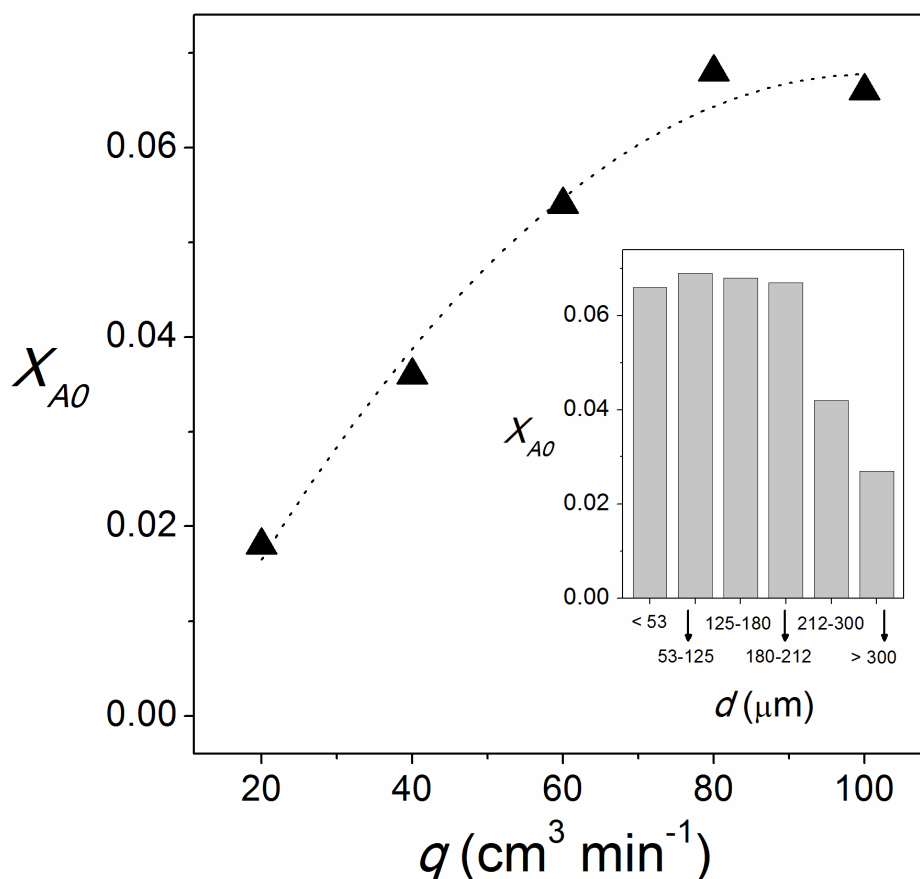

Figure A1: Variation of initial propane fractional conversion (X_{A0}) with the total inlet volumetric flow rate (q) for reaction over Pt-Sn/Al$_2$O$_3$ at $d = 150$ μm. Inset: variation of X_{A0} with the catalyst particle size (d) at $q = 80$ cm^3 min^{-1}. (W/F_{A0}) = 0.04 g h mol^{-1}

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

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

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

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. $\overline{V}_{mix}$ is the molar volume of the fluid:

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

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

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

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

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

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

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

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

where $P_{c,i}$ is the critical pressure of compound i (N m^{-2}). The critical constants ($T_{c,i}$, $P_{c,i}$ and $\overline{V}_{c,i}$) 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

$$\mu_{Propane} = \left(2.40\times10^{-5}\right)\times T + \left(1.35\times10^{-3}\right) \tag{A14}$$

$$\mu_{Propene} = \left(2.82\times10^{-5}\right)\times T + \left(0.48\times10^{-3}\right) \tag{A15}$$

$$\mu_{H_2} = \left(1.34\times10^{-5}\right)\times T + \left(6.20\times10^{-3}\right) \tag{A16}$$

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

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)).

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

$$\overline{\lambda_i} = \left(\lambda_{Eucken1} + \lambda_{Eucken2}\right)/2 \tag{A26}$$

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

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

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

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

$$\left(\frac{h \times d_p}{\lambda_{mix}}\right) = 0.07 \times \mathrm{Re} \qquad\qquad 0.1 < \mathrm{Re} < 10$$

(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

$$\mathrm{Re} = \frac{u_{mix} \times d_p \times \rho_{mix}}{\mu_{mix}} \tag{A37}$$

$$\mathrm{Pr} = \frac{\mu_{mix} \times C_{p,mix}}{\lambda_{mix}} \tag{A38}$$

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

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

$$\left(\frac{k_f \times d_p}{D_{A,mix}}\right) = 0.07 \times \mathrm{Re} \qquad\qquad 0.1 < \mathrm{Re} < 10$$

(A39)

where the Schmidt number (Sc) can be estimated as

$$\mathrm{Sc} = \frac{\mu_{mix}}{\rho_{mix} \times D_{A,mix}} \tag{A40}$$

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

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

$$\Delta \bar{H} = \left(6.97 \times 10^{-9}\right) \times T^3 + \left(-2.69 \times 10^{-5}\right) \times T^2 + \left(3.25 \times 10^{-2}\right) \times T + 116.78 \tag{A42}$$

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

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})

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

where r_0 is the propane consumption rate in mol s^{-1} kg^{-1} and $\rho_{Skeletal}$ = 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

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

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$_2$O$_3$ 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.

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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})	$\mu_{mix} \times 10^5$ (kg m^{-1} s^{-1})	$C_{p,mix}$ (J K^{-1} mol^{-1})	λ_{mix} (J K^{-1} m^{-1} s^{-1})	$D_{A,mix} \times 10^4$ (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×10³	5.131	3.893	3.681	0
C×10⁵	6.011	4.688	-0.772	0
D×10⁸	-7.893	-6.013	0.692	0
E×10¹¹	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 (J K^{-1} m^{-2} s^{-1})	k_f (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