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:

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

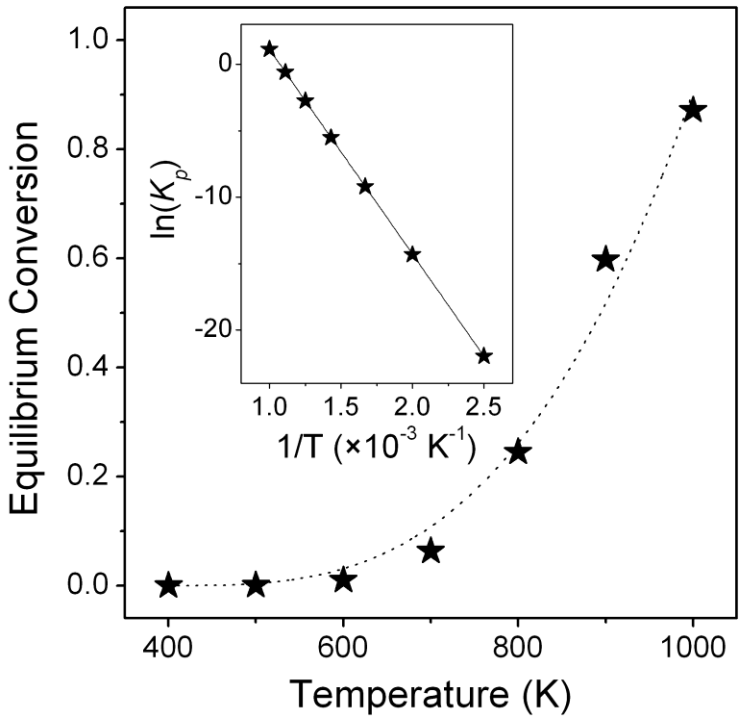

Figure B1: Propane dehydrogenation equilibrium conversion and constant (K_p, inset) as a function of temperature (see eqns. (B.3) and (B.4)).

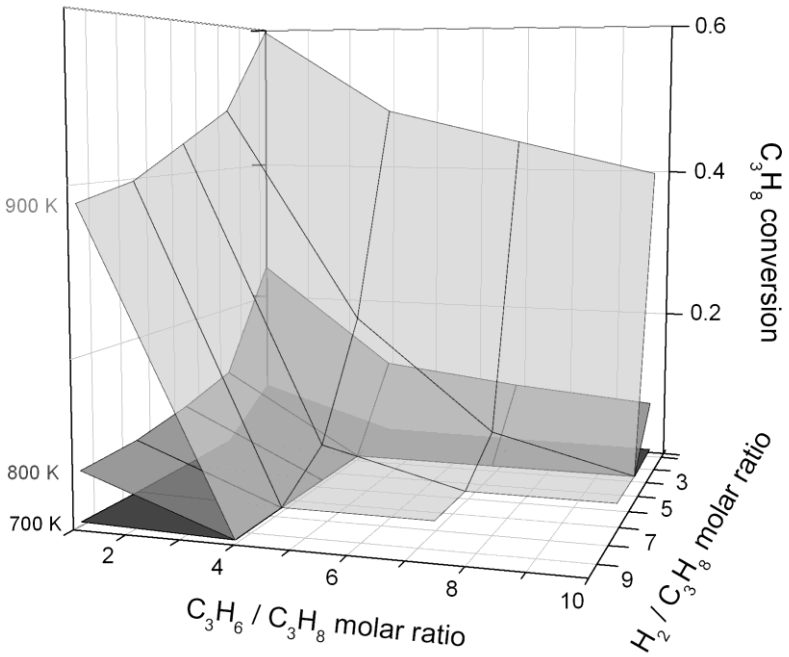

Figure B2: Propane dehydrogenation equilibrium conversion (Z-Axis) as a function of the ratios propylene/propane (X-Axis, left-to-right) and hydrogen/propane (Y-Axis, front-to-back). Each surface represents data calculated at different temperatures (see eqns. (B.6) and (B.7)).