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.\cite{1} We have accordingly analysed the thermodynamics of our case drawing on reference data for propane, propylene and hydrogen as a function of temperature.\cite{2} The specific enthalpy ($\Delta H$) as is given in eqn. (B1). The dehydrogenation of propane is strongly endothermic ($\approx 129 \text{ kJ mol}^{-1}$) within 723 and 823 K.

$$\Delta H = (6.97 \times 10^{-9}) \times T^3 + (-2.69 \times 10^{-5}) \times T^2 + (3.25 \times 10^{-2}) \times T + 116.78 \quad \text{(B1)}$$

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

$$\Delta G = (-0.137) \times T + 128.102 \quad \text{(B2)}$$

$$K_p = (1.48 \times 10^7) \times \exp(-15403/T) \quad \text{(B3)}$$

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

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

Figure B1 presents the results. The maximum achievable fractional conversion in the temperature range studied (723 K $\leq T \leq 823$ K) lies between 0.09 and 0.32. These results are consistent with the works of Michorczyk et al.\cite{3,4} and Assabumrungrat and co-workers.\cite{5} Moreover, Weckhuysen and Schoonheydt reported that temperatures as high as 870 K are needed to achieve a 50% conversion.\cite{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

$$a \text{C}_3\text{H}_8 \leftrightarrow b \text{C}_3\text{H}_6 + c \text{H}_2 \quad \text{(B5)}$$

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

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

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

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 suppress coke formation. 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:

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)).