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:

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

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

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

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:

$$k_2 <<<< k_4, k_9 \quad (C12)$$

$$r_4/k_4 \rightarrow 0, \; r_9/k_9 \rightarrow 0 \quad (C13)$$

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

$$C_{EL} = K_9 \times C_L \times P_E \quad (C14)$$

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

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

The site balance reads then

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

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

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

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

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

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

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

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

$$k_4 <<<< k_2, k_9 \quad (C21)$$

$$r_2/k_2 \rightarrow 0, \; r_9/k_9 \rightarrow 0 \quad (C22)$$

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

$$C_{AL} = K_2 \times C_L \times P_A \quad (C23)$$

$$C_{EL} = K_9 \times C_L \times P_E \quad (C24)$$

The site balance is then

$$C_T = C_L + C_L \times P_A \times K_2 + C_L \times P_E \times K_9 \quad (C25)$$

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

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:

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

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

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

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

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

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

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