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Electronic Supplementary Information

Selective hydrogenation of oleic acid to fatty alcohols over a Rh-Sn-B/Al_2O_3 catalyst. Kinetics and optimal reaction conditions

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The Langmuir-Hinshelwood-Hougen-Watson formalism

Models were developed following the Langmuir-Hinshelwood-Hougen-Watson (LHHW) formalism. Firstly, all the elementary steps of the mechanism must be written down, including components in the fluid phase and components adsorbed over the solid. Especially the surface reaction steps must be detailed. According to the Hougen-Watson treatment, one reaction of the whole reaction mechanism is declared to be rate-limiting. All other reactions are considered in equilibrium. A balance of sites is written and the concentration of adsorbed species are eliminated from this balance by using the equilibrium equations. Finally, equilibrium equations and the sites balance are used to rewrite the rate of the slowest elementary step in terms of known process variables, i.e. partial pressure, concentration in the fluid phase and total concentration of sites. A further lumping of constants into a minimum set of parameters yields the final global rate equation to be used. The adsorption equilibrium and the presence of the solid explicitly leads to rate equations of the Langmuir-Hinshelwood type, thus the branding of the whole procedure as LHHW formalism. This procedure is repeated for each of the global rate equations (r_1 to r_{13}).

Model 8

-All species compete for the same adsorption sites. -One site needed for fatty molecules adsorption. -H_2 adsorption is dissociative. -Acid HDO proceeds in two stages with pairwise H insertion via an aldehyde intermediate. -Pairwise insertion of H for hydrogenation of stearic alcohol and double bonds.

Balance of sites:

$$C_T = C_F + C_{F-H} + C_{F-OAc} + C_{F-OAl} + C_{F-SAl} + C_{F-C18} + C_{F-SAc}$$

$$C_T = C_F + C_F \left[\sqrt{K_{H2} P_{H2}} + K_{OAc} C_{OAc} + K_{OAl} C_{OAl} + K_{SAl} C_{SAl} + K_{SAc} C_{SAc} + K_{C18} C_{C18} \right]$$

$$C_F = \frac{C_T}{1 + \left[\sqrt{K_{H2} P_{H2}} + K_{OAc} C_{OAc} + K_{OAl} C_{OAl} + K_{SAl} C_{SAl} + K_{SAc} C_{SAc} + K_{C18} C_{C18} \right]}$$

$$C_F = C_T \left[\frac{1}{1 + p_6 \sqrt{P_{H2}} + p_7\, C_{OAc} + p_8\, C_{OAl} + p_9\, C_{SAl} + p_{10}\, C_{SAc} + p_{11}\, C_{C18}} \right] = C_T\, \emptyset_F$$

Mechanism of Reactions 1 and 4:

$$2F + H_2 \rightleftarrows 2\,F - H \qquad K_{H2} = \frac{C_{F-H}^2}{C_F^2\, P_{H2}}$$

$$F + OAc \rightleftarrows F - OAc \qquad K_{OAc} = \frac{C_{F-OAc}}{C_F\, C_{OAc}}$$

$$2\,F - H + F - OAc \rightleftarrows 2\,F + F - OAld + H_2O \qquad r_1 = k\, C_{F-H}^2\, C_{F-OAc}$$

$$F - OAld + 2\,F - H \rightleftarrows 2\,F + F - OAl \qquad K_{Ald} = \frac{{C_F}^2 C_{F-OAl}}{C_{F-OAld}\, C_{F-H}^2}$$

$$F + OAl \rightleftarrows F - OAl \qquad K_{OAl} = \frac{C_{F-OAl}}{C_{OAl}\, C_F}$$

$$r_1 = k_1\, C_{F-H}^2\, C_{F-OAc} = k_1\, (K_{H2}\, C_F^2\, P_{H2})(K_{OAc}\, C_F\, C_{OAc}) = \left(k_1\, {C_T}^3 K_{H2}\, K_{OAc}\right) {\emptyset_F}^3 P_{H2} C_{OAc} = p_1\, {\emptyset_F}^3 P_{H2} C_{OAc}$$

$$r_4 = \left(k_4\, {C_T}^3 K_{H2}\, K_{SAc}\right) {\emptyset_F}^3 P_{H2} C_{SAc} = p_4\, {\emptyset_F}^3 P_{H2}\, C_{SAc}$$

The concentration of adsorbed aldehyde intermediate is considered to be negligible, i.e. the reaction of hydrogenation of the adsorbed aldehyde is considered to be very fast and irreversible. Water has very little solubility in the solvent and segregates from the reaction medium. Then its concentration is assumed constant and equal to the solubility value.

Mechanism of Reactions 2 and 3:

$$2F + H_2 \rightleftarrows 2\,F - H \qquad K_{H2} = \frac{C_{F-H}^2}{C_F^2\, P_{H2}}$$

$F + OAc \rightleftarrows F - OAc$ $\qquad K_{OAc} = \frac{C_{F-OAc}}{C_F\, C_{OAc}}$

$2\,F - H + F - OAc \rightleftarrows 2\,F + F - SAc$ $\qquad r_2 = k_2\, C_{F-H}^2\, C_{F-OAc}$

$F + SAc \rightleftarrows F - SAc$ $\qquad K_{SAc} = \frac{C_{F-SAc}}{C_{SAc}\, C_F}$

$$r_2 = k_2\, C_{F-H}^2\, C_{F-OAc} = k_2\,(K_{H2}\, C_F^2\, P_{H2})(K_{OAc}\, C_F\, C_{OAc}) = \left(k_2\, {C_T}^3 K_{H2}\, K_{OAc}\right) {\emptyset_F}^3 P_{H2} C_{OAc} = p_2\, {\emptyset_F}^3 P_{H2}\, C_{OAc}$$

$$r_3 = k_3\, C_{F-H}^2\, C_{F-OAl} = k_3\,(K_{H2}\, C_F^2\, P_{H2})(K_{OAl}\, C_F\, C_{OAl}) = \left(k_3\, {C_T}^3 K_{H2}\, K_{OAl}\right) {\emptyset_F}^3 P_{H2} C_{OAl} = p_3\, {\emptyset_F}^3 P_{H2}\, C_{OAl}$$

Mechanism of Reaction 5:

$2\,F + H_2 \rightleftarrows 2\,F - H$ $\qquad K_{H2} = \frac{C_{F-H}^2}{C_F^2\, P_{H2}}$

$F + SAl \rightleftarrows F - SAl$ $\qquad K_{SAl} = \frac{C_{F-SAl}}{C_F\, C_{SAl}}$

$2\,F - H + F - SAl \rightleftarrows 2\,F + F - C_{18} + H_2O$ $\qquad r_2 = k_5\, C_{F-H}^2\, C_{F-SAl}$

$F + C_{18} \rightleftarrows F - C_{18}$ $\qquad K_{SAc} = \frac{C_{F2-SAl}}{C_{SAl} {C_F}^2}$

$$r_5 = k_5\, C_{F-H}^2\, C_{F-SAl} = k_5\,(K_{H2}\, C_F^2\, P_{H2})(K_{SAl}\, C_F\, C_{SAl}) = \left(k_5\, {C_T}^3 K_{H2}\, K_{SAl}\right) {\emptyset_F}^3\, P_{H2}\, C_{SAl} = p_5\, {\emptyset_F}^3 P_{H2}\, C_{SAl}$$

Model 9 is obtained from Model 8 by making P_8=P_9=P_{10}=P_{11}=0, i.e. by disregarding the influence of the minor adsorbates in the adsorption term of the rate equation.

Model 28

-All species compete for the same adsorption sites. -Two sites needed for fatty molecule adsorption. -H_2 adsorption is molecular and needs two sites. -Acid HDO proceeds in two stages with pairwise H insertion via an aldehyde intermediate. -Pairwise insertion of H for hydrogenation of stearic alcohol and double bonds. -Group specific rate constants. -All adsorption terms considered.

Balance of sites:

$$C_T = C_{\mathrm{F}} + C_{\mathrm{F-H2}} + C_{F_2-OAc} + C_{F_2-OAl} + C_{F_2-SAl} + C_{F_2-C18} + C_{F_2-SAc}$$

$$C_T = C_{\mathrm{F}} + {C_F}^2[\, K_{H2}P_{H2} + K_{\mathrm{OAc}}C_{OAc} + K_{\mathrm{OAl}}C_{OAl} + K_{\mathrm{SAl}}C_{SAl} + K_{\mathrm{C18}}C_{C18} + K_{\mathrm{SAc}}C_{SAc}\,]$$

$$1 = \emptyset_{\mathrm{F}} + {\emptyset_F}^2[\, C_T K_{H2}P_{H2} + C_T K_{\mathrm{OAc}}C_{OAc} + C_{\mathrm{T}}K_{OAl}C_{OAl} + C_{\mathrm{T}}K_{SAl}C_{SAl} + C_{\mathrm{T}}K_{C18}C_{C18} + C_{\mathrm{T}}K_{SAc}C_{SAc}\,]$$

$$1 = \emptyset_{\mathrm{F}} + {\emptyset_F}^2[\, p_6 P_{H2} + p_7 C_{OAc} + p_8 C_{OAl} + p_9 C_{SAl} + p_{10} C_{C18} + p_{11} C_{SAc}\,]$$

$$\emptyset_F = \varphi(P_{H2}, C_{OAc}, C_{OAl}, C_{SAl}, C_{C18}, C_{SAc}, p_6 \dots p_{11})$$

Mechanism of Reactions 1 and 4:

$$2F + H_2 \rightleftarrows F_2 - H_2 \qquad K_{H2} = \frac{C_{\mathrm{F2-H2}}}{{C_{\mathrm{F}}}^2\, P_{H2}}$$

$$2F + OAc \rightleftarrows F_2 - OAc \qquad K_{OAc} = \frac{C_{F_2-\mathrm{OAc}}}{{C_{\mathrm{F}}}^2\, C_{OAc}}$$

$$F_2 - H_2 + F_2 - OAc \rightleftarrows F + F_2 - OAld + H_2O \qquad r_1 = kC_{F2-H2}C_{F2-OAc}$$

$$F_2 - OAld + F_2 - H_2 \rightleftarrows 2F + F_2 - OAl \qquad K_{Ald} = \frac{{C_F}^2 C_{F2-OAl}}{C_{F2-OAld}C_{F2-H2}}$$

$$2F + OAl \rightleftarrows F_2 - OAl \qquad K_{OAl} = \frac{C_{F2-OAl}}{C_{OAl}{C_F}^2}$$

$$r_1 = kC_{F-H2}C_{F2-OAc} = k\,(K_H C_F^2 P_{H2})\big(K_{OAc}\, {C_F}^2\, C_{OAc}\big) = p_1 {C_F}^4 P_{H2} C_{OAc}$$

$$r_4 = p_4 {C_F}^4 P_{H2} C_{SAc}$$

The concentration of adsorbed aldehyde intermediate is considered to be negligible, i.e. the reaction of hydrogenation of the adsorbed aldehyde is considered to be very fast and irreversible. Water has very little solubility in the solvent and segregates from the reaction medium. Then its concentration is assumed constant and equal to this solubility value.

Mechanism of Reactions 2 and 3:

$$2F + H_2 \rightleftarrows F_2 - H_2 \qquad K_{H2} = \frac{C_{\mathrm{F2-H2}}}{{C_{\mathrm{F}}}^2\, P_{H2}}$$

$$2F + OAc \rightleftarrows F_2 - OAc \qquad K_{OAc} = \frac{C_{F_2-\mathrm{OAc}}}{{C_{\mathrm{F}}}^2\, C_{OAc}}$$

$F_2 - H_2 + F_2 - OAc \rightleftarrows 2F + F_2 - SAc$ $\qquad r_2 = kC_{F2-H2}C_{F2-OAc}$

$2F + SAc \rightleftarrows F_2 - SAc$ $\qquad K_{SAc} = \frac{C_{F2-SAc}}{C_{SAc}C_F{}^2}$

$$r_2 = kC_{F-H2}C_{F2-OAc} = k\left(K_{H2}C_\mathrm{F}{}^2P_{H2}\right)\left(K_{OAc}C_\mathrm{F}{}^2\,C_{OAc}\right) = p_2C_F{}^4P_{H2}C_{OAc}$$

$$r_3 = p_3C_F{}^4P_{H2}C_{OAl}$$

Mechanism of Reaction 5:

$2F + H_2 \rightleftarrows F_2 - H_2$ $\qquad K_{H2} = \frac{C_{\mathrm{F2-H2}}}{C_\mathrm{F}{}^2\,P_{H2}}$

$2F + SAl \rightleftarrows F_2 - SAl$ $\qquad K_{OAc} = \frac{C_{F_2-\mathrm{SAl}}}{C_\mathrm{F}{}^2\,C_{SAl}}$

$F_2 - H_2 + F_2 - SAl \rightleftarrows 2\,F + F_2 - C_{18} + H_2O$ $\qquad r_2 = k\,C_{F2-H2}\,C_{F2-SAl}$

$2F + C_{18} \rightleftarrows F_2 - C_{18}$ $\qquad K_{SAc} = \frac{C_{F2-C18}}{C_{C18}C_F{}^2}$

$$r_5 = kC_{F-H2}C_{F2-SAl} = k\left(K_{H2}C_\mathrm{F}{}^2P_{H2}\right)\left(K_{SAl}C_\mathrm{F}{}^2C_{SAl}\right) = p_5C_F{}^4P_{H2}C_{SAl}$$

Model 31

-All species compete for the same adsorption sites. -Two sites needed for fatty molecule adsorption. -H_2 adsorption is molecular and needs only one site. -Acid HDO proceeds in two stages with pairwise H insertion via an aldehyde intermediate. -Pairwise insertion of H for hydrogenation of stearic alcohol and double bonds. -Group specific rate constants. -Concentration of some adsorbates is disregarded, only oleic acid, oleyl alcohol and stearyl alcohol considered.

$$C_\mathrm{T} = C_\mathrm{F} + C_\mathrm{F}K_{H2}P_{H2} + C_\mathrm{F}{}^2[\,K_{OAc}C_{OAc} + K_{OAl}C_{OAl} + K_{SAl}C_{SAl} + K_{SAc}C_{SAc} + K_{C18}C_{C18}\,]$$

$1 = \emptyset_\mathrm{F} + \emptyset_F{}^2[\,p_6C_{OAc} + p_7C_{OAl} + p_8C_{SAl}\,]$ (only oleic acid, oleyl alcohol and stearyl alcohol considered as adsorbates)

$$r_1 = kC_{F-H2}C_{F2-OAc} = k\,(K_HC_FP_{H2})\left(K_{OAc}C_\mathrm{F}{}^2\,C_{OAc}\right) = p_1C_F{}^3P_{H2}C_{OAc}$$

$$r_3 = p_3C_F{}^3P_{H2}C_{OAl}$$

$$r_5 = kC_{F-H2}C_{F2-SAl} = k\,(K_{H2}C_FP_{H2})\left(K_{SAl}C_\mathrm{F}{}^2\,C_{SAl}\right) = p_5C_F{}^3P_{H2}C_{SAl}$$