

Supporting Information

General kinetic modeling of the selective hydrogenation of 2-methyl-3-butyn-2-ol over a commercial palladium-based catalyst

Sergio Vernuccio and Philipp Rudolf von Rohr*

Institute of Process Engineering, ETH Zurich, Sonneggstrasse 3, 8092 Zurich, Switzerland

Jonathan Medlock

DSM Nutritional Products, Research and Development, Basel, Switzerland

Corresponding Author E-mail: svernuccio@ipe.mavt.ethz.ch

Physical properties

Some of the catalyst characteristics are summarized in Tab. S1. The cumulative distribution function of particle sizes was measured by laser diffraction (HELOS BR, Sympatec, Germany). The catalyst density was assumed to be equal to the density of CaCO₃ used as support.

Table S1. Catalyst characteristics

Property	Value
Cumulative particles size distribution μm	< 60 for 100 %
	< 43 for 83 %
	< 36 for 72 %
	< 22 for 50 %
	< 9 for 30 %
	< 4 for 18 %
	< 1 for 6 %
BET surface area $\text{m}^2 \cdot \text{g}^{-1}$	1.2
Density, ρ_s ¹ $\text{kg} \cdot \text{m}^{-3}$	2710

The physical properties of MBY, measured by DSM Nutritional Products at Kaiseraugst/Switzerland are listed in Tab. S2.

Table S2. Physical properties of MBY

T K	Density, ρ_L $\text{kg} \cdot \text{m}^{-3}$	Viscosity, $\mu_L \cdot 10^3$ Pa·s	Vapor pressure, p^0 bar
313	843	1.79	0.05
333	821	1.04	0.16
343	809	0.82	0.25
353	798	0.66	0.39

Determination of the kinetic model

A Langmuir-Hinshelwood mechanism was developed assuming non-competitive adsorption of hydrogen and organics on the catalyst surface. The different active sites of the catalyst are indicated with the symbols “□” for hydrogen and “○” for organics respectively. The adsorption-desorption steps were assumed to be reversible. The elementary steps considered for the three reactions involved in the MBY hydrogenation network are listed below. The species R , P , Q' , Q'' and Q''' represent partially hydrogenated radicals.

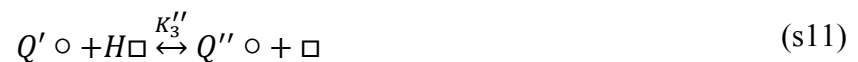
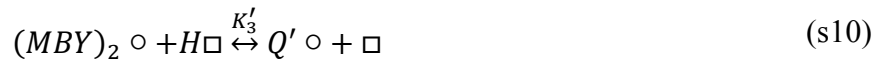
Reaction 1: MBY hydrogenation to MBE



Reaction 2: MBE hydrogenation to MBA



Reaction 3: Dimers formation





The equilibrium constants can be expressed as

$$K_Y = \frac{\vartheta_Y}{C_Y \vartheta_0} \quad (\text{s15})$$

$$K_H = \frac{\vartheta_H'^2}{C_H \vartheta_0'^2} \quad (\text{s16})$$

$$K_\phi = \frac{\vartheta_{Y_2}}{C_Y \vartheta_Y} \quad (\text{s17})$$

$$K_E = \frac{\vartheta_E}{C_E \vartheta_0} \quad (\text{s18})$$

$$K_A = \frac{\vartheta_A}{C_A \vartheta_0} \quad (\text{s19})$$

$$K_D = \frac{\vartheta_D}{C_D \vartheta_0} \quad (\text{s20})$$

Considering the last hydrogen addition as the rate determining step for each of the three reactions, it results

$$K_1' = \frac{\vartheta_R \vartheta_0'}{\vartheta_Y \vartheta_H'} \quad (\text{s21})$$

$$r_1' = k_1' \vartheta_R \vartheta_H' \quad (\text{s22})$$

$$K_2' = \frac{\vartheta_P \vartheta_0'}{\vartheta_E \vartheta_H'} \quad (\text{s23})$$

$$r_2' = k_2' \vartheta_P \vartheta_H' \quad (\text{s24})$$

$$K_3' = \frac{\vartheta_{Q'} \vartheta_0'}{\vartheta_{Y_2} \vartheta_H'} \quad (\text{s25})$$

$$K_3'' = \frac{\vartheta_{Q''} \vartheta_0'}{\vartheta_{Q'} \vartheta_H'} \quad (\text{s26})$$

$$K_3''' = \frac{\vartheta_{Q'''} \vartheta_0'}{\vartheta_{Q''} \vartheta_H'} \quad (\text{s27})$$

$$r'_3 = k'_3 \vartheta_{Q'''} \vartheta'_H \quad (\text{s28})$$

The mass balances on the catalyst active sites are expressed as follows (the fraction of active sites covered with the semi-hydrogenated radicals is neglected)

$$\vartheta_Y + \vartheta_E + \vartheta_A + \vartheta_D + \vartheta_{Y_2} + \vartheta_0 = 1 \quad (\text{s29})$$

$$\vartheta'_H + \vartheta'_0 = 1 \quad (\text{s30})$$

Combining equations (s16) and (s30) it results

$$\vartheta'_0 = \frac{1}{1 + \sqrt{K_H C_H}} \quad (\text{s31})$$

$$\vartheta'_H = \frac{\sqrt{K_H C_H}}{1 + \sqrt{K_H C_H}} \quad (\text{s32})$$

With the same approach, combining the expression of the other equilibrium constants with the mass balance (s29), it results

$$\vartheta_0 = \frac{1}{1 + K_Y C_Y (1 + K_\varphi C_Y) + K_E C_E + K_A C_A + K_D C_D} \quad (\text{s33})$$

$$\vartheta_R = \frac{K'_1 K_Y C_Y \sqrt{K_H C_H}}{1 + K_Y C_Y (1 + K_\varphi C_Y) + K_E C_E + K_A C_A + K_D C_D} \quad (\text{s34})$$

$$\vartheta_P = \frac{K'_2 K_E C_E \sqrt{K_H C_H}}{1 + K_Y C_Y (1 + K_\varphi C_Y) + K_E C_E + K_A C_A + K_D C_D} \quad (\text{s35})$$

$$\vartheta_{Q'''} = \frac{K'_3 K''_3 K'''_3 K_Y K_\varphi C_Y^2 K_H C_H \sqrt{K_H C_H}}{1 + K_Y C_Y (1 + K_\varphi C_Y) + K_E C_E + K_A C_A + K_D C_D} \quad (\text{s36})$$

The following expressions for the reaction rates are finally deduced

$$r_1 = k'_1 \vartheta_R \vartheta'_H = k'_1 K'_1 \frac{K_Y C_Y}{1 + K_Y C_Y (1 + K_\varphi C_Y) + K_E C_E + K_A C_A + K_D C_D} \cdot \frac{K_H C_H}{1 + \sqrt{K_H C_H}} \quad (\text{s37})$$

$$r_2 = k'_2 \vartheta_P \vartheta'_H = k'_2 K'_2 \frac{K_E C_E}{1 + K_Y C_Y (1 + K_\varphi C_Y) + K_E C_E + K_A C_A + K_D C_D} \cdot \frac{K_H C_H}{1 + \sqrt{K_H C_H}} \quad (\text{s38})$$

$$\begin{aligned}
r_3 &= k_3' \vartheta_{Q'''} \vartheta_H' \\
&= k_3' K_3' K_3'' K_3''' \frac{K_Y K_\varphi C_Y^2}{1 + K_Y C_Y (1 + K_\varphi C_Y) + K_E C_E + K_A C_A + K_D C_D} \\
&\quad \cdot \frac{K_H^2 C_H^2}{1 + \sqrt{K_H C_H}}
\end{aligned} \tag{s39}$$

Supporting References

- (1) Liley, P. E.; Thompson, G. H.; Friend D. G.; Daubert, T. E.; Buck, E. Physical and chemical data. In *Perry's Chemical Engineers' Handbook*, ed. 8. D. W. Green, ed. New York; McGraw-Hill, 2008.