

Supporting Information

Kinetic study of liquid phase glycerol hydrodeoxygenation under inert conditions over Cu-based catalyst

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Catalyst characterization:

The surface area of the fresh calcined sample was determined by N₂ adsorption at –469K using a multipoint BET analysis method with an Autosorb-1 Quantachrome flow apparatus. Prior to the measurements, the samples were treated under vacuum at 523K overnight.

The reduction characteristics of the catalysts (Figure S1) were studied by temperature-programmed reduction (TPR). These experiments were performed in a gas flow system equipped with a quadrupole mass analyser (OmniStar™, PFEIFFER). Typically, a catalyst sample (100 mg) was placed in a U-shaped quartz reactor and pre-treated in flowing He for 0.5 h at 523K, followed by cooling at room temperature. After the pre-treatment, the temperature was raised from room temperature to 773K at a rate of 10 K min⁻¹ in a 10% H₂/He flow.

The active copper metal surface area was determined by a dissociative N₂O adsorption method. The experiment was performed in a gas flow system equipped with a quadrupole mass analyzer (OmniStar™, PFEIFFER). Typically, a fresh catalyst sample (150 mg) was placed in a U-shaped quartz reactor and pre-treated in flowing He for 0.5 h at 523K, followed by cooling at room temperature. Catalyst pre-reduction was performed by raising the temperature to the reduction temperature (543K) at a ramp rate of 10 °C min⁻¹ in a 10% H₂/He flow for 0.5 h, followed by cooling to 323K under He flow. Then, the sample was exposed to N₂O flow for 0.5 h at 323K in order to oxidize the surface CuO to Cu₂O by adsorptive decomposition of N₂O. Finally, TPR was carried out on the freshly oxidized Cu₂O surface in order to reduce Cu₂O to metallic Cu, increasing the temperature from room to 723K with 10 °C min⁻¹ ramp rate using 10% H₂/He flow. Copper surface area and particle size was calculated using data adopted from the literature [G. Ertl, H. Knozinger and J. Weitkamp, Handbook of Heterogeneous Catalysis, Wiley-VCH, Germany, 1997, vol. 2.].

The diffractogram of the catalyst (Figure S2) was obtained using a Siemens D500 diffractometer with Cu K α radiation.

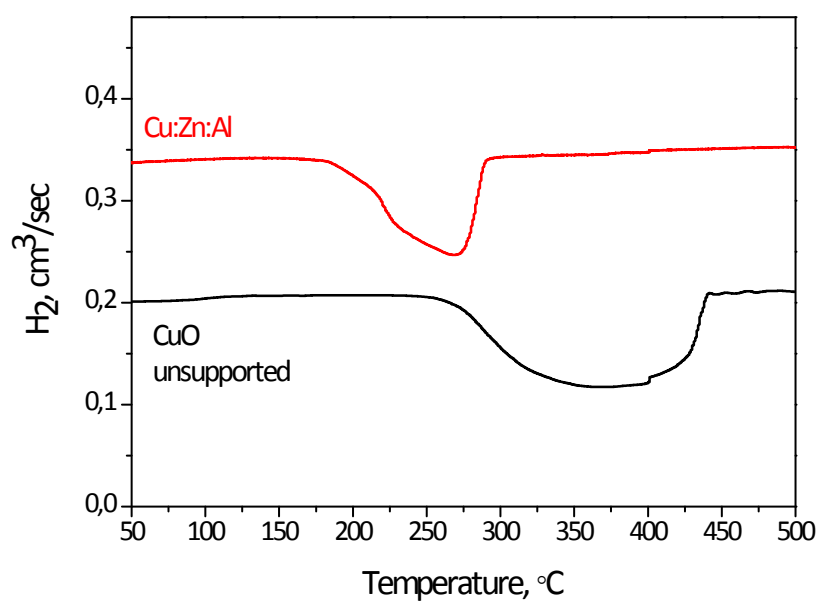


Figure S1: TPR patterns of the Cu:Zn:Al catalyst and CuO unsupported oxide

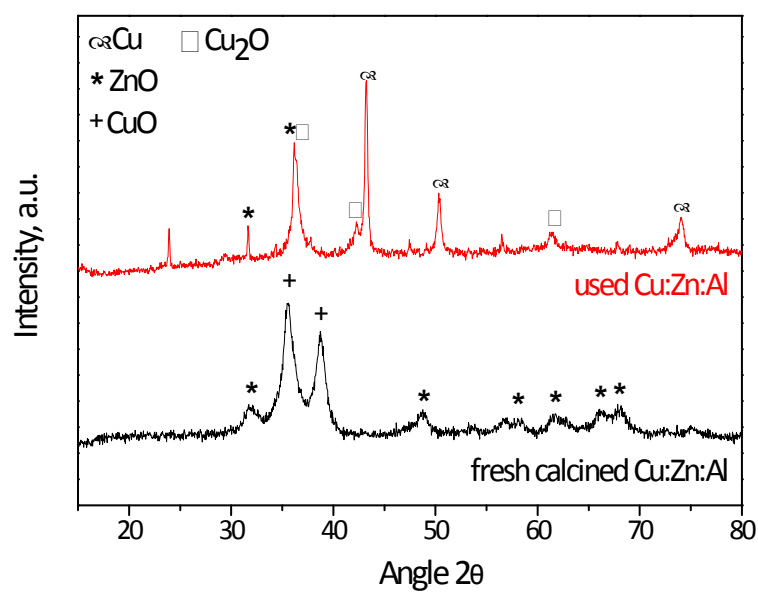


Figure S2: XRD patterns of the fresh calcined and used Cu:Zn:Al catalyst

Weisz – Prater criterion

The Weisz – Prater parameter was calculated by using the following equation:

$$C_{WP} = \frac{-r_{obs} \cdot \rho_c \cdot R^2}{De \cdot C_{AS}}$$

where, $-r_{obs}$ = the observed reaction rate = $6.92 \cdot 10^{-6} \text{ mol g}_{cat}^{-1} \text{ sec}^{-1}$,

ρ_c = solid catalyst density = 2.08 g cm^{-3} ,

R = catalyst particle radius = 0.0025 cm ,

C_{AS} = concentration of glycerol at catalyst surface = $1.3 \cdot 10^{-4} \text{ mol cm}^{-3}$.

$$1) De = \frac{D_{AB} \cdot \phi \cdot \sigma}{\tau} \quad \text{effective diffusivity of glycerol to water at 523K} = 2.11 \cdot 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}$$

$$2) De = \frac{D_{AB} \cdot \phi \cdot \sigma}{\tau} \quad \text{effective diffusivity of glycerol to methanol at 523K} = 4.81 \cdot 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}$$

where,

$\phi = 0.42$ pellet porosity, $\sigma = 0.8$ constriction factor [Fogler], $\tau = 3$ tortuosity [Fogler]

The diffusion coefficient was calculated using the WILKE – CHANG equation:

$$1) D_{AB} = \text{diffusion coefficient of glycerol to water at 523K} = 1.85 \cdot 10^{-4} \text{ cm}^2 \cdot \text{sec}^{-1}$$

$$2) D_{AB} = \text{diffusion coefficient of glycerol to methanol at 523K} = 4.20 \cdot 10^{-4} \text{ cm}^2 \cdot \text{sec}^{-1}$$

Values of Weisz – Prater parameter:

$$C_{WP \text{ GLYCEROL - WATER}} = 0.033 < 1$$

$$C_{WP \text{ GLYCEROL - METHANOL}} = 0.014 < 1$$

Mears criterion

$$C_{mears} = \frac{-r_A p_b R n}{k_c C_{Ab}}$$

$-r_A$ = the observed reaction rate = $6.92 \cdot 10^{-6} \text{ mol g}_{\text{cat}}^{-1} \text{ sec}^{-1}$

n = reaction order = 1

R = catalyst particle radius = 0.0025 cm,

p_b = bulk density = $1.19 \text{ gr} \cdot \text{cm}^{-3}$

C_{AS} = concentration of glycerol in solution = $1.3 \cdot 10^{-4} \text{ mol cm}^{-3}$

$$1) k_c = \frac{Sh \cdot D_{AB}}{d_p} \quad \text{mass transfer coefficient glycerol - water = m/s}$$

$Sh = 2 + 0.6 \cdot Re^{0.5} \cdot Sc^{1/3}$ = Sherwood number = 23.1

$Sc = \nu / D_{AB}$ = Schmidt number = 7.36

ν = kinetic viscosity of water at 523K = $1.36 \cdot 10^{-3} \text{ cm}^2/\text{s}$

D_{AB} = diffusion coefficient of glycerol to water at 523K = $1.85 \cdot 10^{-4} \text{ cm}^2 \cdot \text{sec}^{-1}$

$$Re = \frac{U \cdot \rho \cdot d_p}{\mu} \quad \text{Reynolds number} = 326.4$$

U = superficial velocity = 0.89 m/s

ρ = density of water at 523K = $799 \text{ kg} \cdot \text{m}^{-3}$

μ = dynamic viscosity of water at 523K = $1.1 \cdot 10^{-4} \text{ kg} \cdot \text{s}^{-1} \cdot \text{m}^{-1}$

d_p = catalyst particle diameter = $5 \cdot 10^{-5} \text{ m}$

$$2) k_c = \frac{Sh \cdot D_{AB}}{d_p} \quad \text{mass transfer coefficient glycerol - methanol = m/s}$$

$$\mathbf{Sh} = 2 + 0.6 \cdot \text{Re}^{0.5} \cdot \text{Sc}^{1/3} = \text{Sherwood number} = 16.8$$

$$\mathbf{Sc} = \nu / D_{AB} = \text{Schmidt number} = 5.2$$

$$\nu = \text{kinetic viscosity of methanol at 523K} = 2.2 \cdot 10^{-3} \text{ cm}^2/\text{s}$$

$$D_{AB} = \text{diffusion coefficient of glycerol to methanol at 523K} = 4.2 \cdot 10^{-4} \text{ cm}^2 \cdot \text{sec}^{-1}$$

$$\text{Re} = \frac{U \cdot \rho \cdot d_p}{\mu} \quad \text{Reynolds number} = 203.5$$

$$U = \text{superficial velocity} = 0.89 \text{ m/s}$$

$$\rho = \text{density of water at 523K} = 250 \text{ kg} \cdot \text{m}^{-3}$$

$$\mu = \text{dynamic viscosity of water at 523K} = 5.5 \cdot 10^{-5} \text{ kg} \cdot \text{s}^{-1} \cdot \text{m}^{-1}$$

$$d_p = \text{catalyst particle diameter} = 5 \cdot 10^{-5} \text{ m}$$

Values of Mears criterion

$$1) \frac{-r_A \rho_b R n}{k_c C_{Ab}}_{\text{GLYCEROL - WATER}} = 1.85 \cdot 10^{-4} < 0.15$$

$$2) \frac{-r_A \rho_b R n}{k_c C_{Ab}}_{\text{GLYCEROL - METHANOL}} = 1.12 \cdot 10^{-4} < 0.15$$

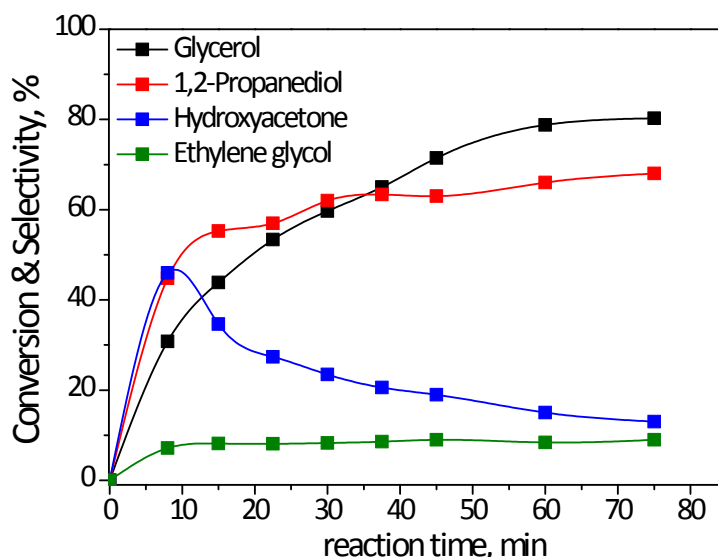


Figure S3: Effect of reaction time on glycerol conversion and product selectivity. Experimental conditions: aq. solution of 1wt% glycerol and 30wt% methanol, $m_{\text{glycerol}}/m_{\text{catalyst}} = 2.4$, 3.0MPa N_2 523K, 0-75min.

RDS selection

Case 1 (hydrogen formation RDS = the dehydrogenation of methoxy species to formaldehyde).

The overall reactions that describe the four reaction steps along with the resulting four rate equations are presented in Table S1. The parity plots for each reaction compound are depicted in Figure S1.

Table S1: Elementary reactions and rate equations (Case 1)

	Elementary reactions	Rate equations
1st step - H ₂ formation	$H_2O + * \leftrightarrow H_2O^*$ $H_2O^* + * \leftrightarrow OH^* + H^*$ $CH_3OH + 2* \leftrightarrow CH_3O^* + H^*$ $CH_3O^* + * \rightarrow CH_2O^* + H^*$ RDS_1 : $CO^* + OH^* \rightarrow H^* + CO_2$ $2H^* \leftrightarrow H_2 + 2*$	$r_1 = \frac{k_1 K_{CH_3OH} C_{CH_3OH} (K_{H_2} C_{H_2})^{-0.5}}{(DEN)^2}$
2nd step - Hydroxyacetone formation	$G + * \leftrightarrow G^*$ $G^* + * \rightarrow HA^* + H_2O^*$ RDS_2 $HA^* \leftrightarrow HA + *$	$r_2 = \frac{k_2 K_G C_G}{(DEN)^2}$
3rd step - 1,2-propanediol formation	$HA^* + H^* \rightarrow HAH^* + *$ $HAH^* + H^* \leftrightarrow 1,2-PDO^* + *$ RDS_3	$r_3 = k_3 \frac{K_{HAH} K_{HA} K_{H_2} C_{H_2} - K_{PG} C_{PG}}{(DEN)^2}$

	1,2-PDO* \leftrightarrow 1,2-PDO + *	
4th step – ethylene glycol formation	$G^* + H^* \rightarrow GH^* + *$ RDS_4 $GH^* + H^* \rightarrow EG^* + CH_3OH^*$ $EG^* \leftrightarrow EG + *$	$r_4 = \frac{k_4 K_G C_G (K_{H_2} C_{H_2})^{0.5}}{(DEN)^2}$
* = active site, G = glycerol, 1,2-PDO = 1,2-propanediol, EG = ethylene glycol, HA = hydroxyacetone, H = hydrogen		

Where,

$$DEN = 1 + K_G C_G + K_{CH_3OH} C_{CH_3OH} (K_{H_2} C_{H_2})^{-0.5} + K_{HA} C_{HA} + K_{PG} C_{PG} + (K_{H_2} C_{H_2})^{0.5} + K_{HAH} K_{HA} C_{HA} (K_{H_2} C_{H_2})^{0.5}$$

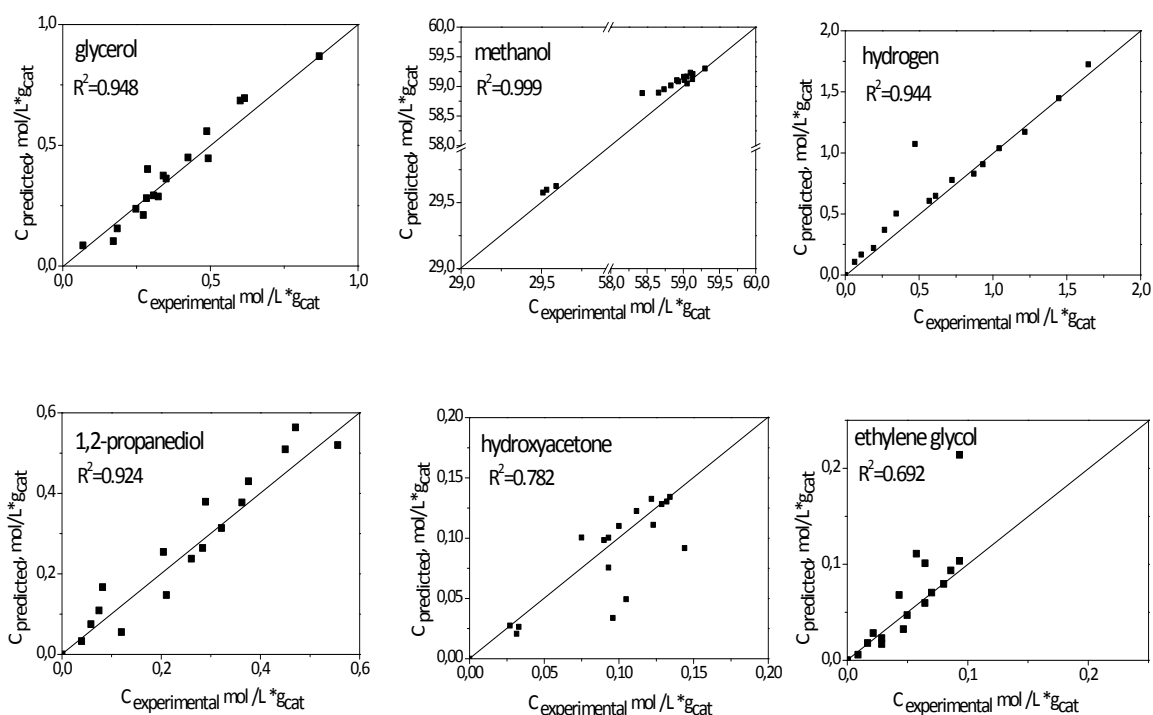


Figure S4: Parity plots of experimental and predicted (from the reaction model) values of reactants and products outlet concentrations – Case 1. Experimental conditions: aq. solution of 1wt% glycerol and 30wt% methanol, $m_{glycerol}/m_{catalyst} = 2.4$, 3.0MPa N_2 , 473-543K, 0-75min.

Case 2: (Hydroxyacetone hydrogenation to 1,2-propanediol is one-step irreversible reaction).

The overall reactions that describe the four reaction steps along with the resulting four rate equations are presented in Table S2. The results of the model are presented in Figure S5 as outlet concentration – time curves while in Table S3 are tabulated the values of all kinetic parameters, equilibrium and adsorption coefficients at 523K. The residual sum of squares in case 1 was 0.29.

Table S2: Elementary reactions and rate equations (Case 2)

	Elementary reactions	Rate equations
1st step - H ₂ formation	H ₂ O + * ⇌ H ₂ O* H ₂ O* + * ⇌ OH* + H* CH ₃ OH + * ⇌ CH ₃ OH* CH₃OH* + * → CH₃O* + H* RDS_1 : CO* + OH* → H* + CO ₂ 2H* ⇌ H ₂ + 2*	$r_1 = k_1 \frac{K_{CH_3OH} C_{CH_3OH}}{(DEN)^2}$
2nd step - Hydroxyacetone formation	G + * ⇌ G* G* + * → HA* + H₂O* RDS_2 HA* ⇌ HA + *	$r_2 = k_2 \frac{K_G C_G}{(DEN)^2}$
3rd step - 1,2-propanediol formation	HA* + 2H* → 1,2-PDO* + 2* RDS_3 1,2-PDO* ⇌ 1,2-PDO + *	$r_3 = k_3 \frac{K_{HA} C_{HA} K_{H_2} C_{H_2}}{(DEN)^3}$
4th step - ethylene glycol formation	G* + H* → GH* + * RDS_4 GH* + H* → EG* + CH ₃ OH* EG* ⇌ EG + *	$r_4 = k_4 \frac{K_G C_G (K_{H_2} C_{H_2})^{0.5}}{(DEN)^2}$
*=active site, G=glycerol, 1,2-PDO=1,2-propanediol, EG=ethylene glycol, HA=hydroxyacetone, H =hydrogen		

Where,

$$DEN = 1 + K_G C_G + K_{CH_3OH} C_{CH_3OH} + K_{HA} C_{HA} + K_{PG} C_{PG} + (K_{H_2} C_{H_2})^{0.5}$$

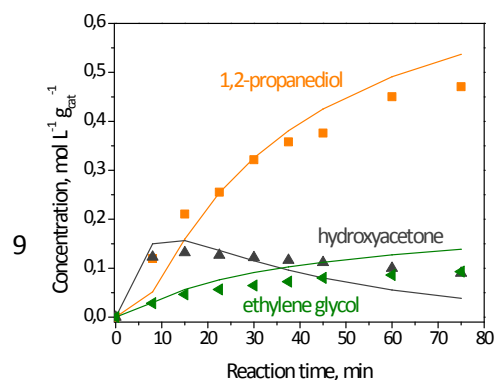
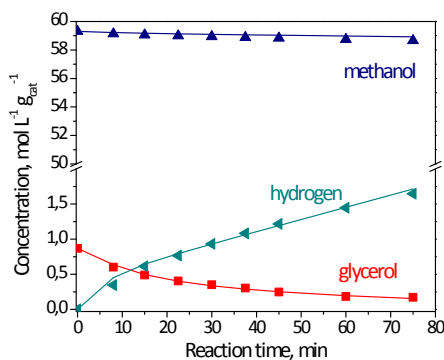


Figure S5: Experimental (points) and predicted (lines) values of reactants and products outlet concentrations as a function of reaction time (Case 2). Experimental conditions: aq. solution of 1wt% glycerol and 30wt% methanol, $m_{\text{glycerol}}/m_{\text{catalyst}} = 2.4$, , 3.0MPa N_2 , 523 K, 0-75min.

Table S3: Estimated values of kinetic parameters (Case 2)

Kinetic parameters	Step 1) Methanol APR	Step 2) Glycerol dehydration	Step 3) Hydroxyacetone hydrogenation	Step 4) Glycerol hydrogenolysis
k_i, min^{-1} (523K)	$1.6 \cdot 10^6$	$1.9 \cdot 10^7$	$2.0 \cdot 10^{10}$	$1.4 \cdot 10^7$

Adsorption coefficients					
	Methanol	Glycerol	1,2-propanediol	Hydroxyacetone	Hydrogen
$K_j, g_{\text{cat}} \cdot L \cdot \text{mol}^{-1}$ (523K)	$1.1 \cdot 10^{-4}$	$1.4 \cdot 10^{-3}$	$9.9 \cdot 10^{-1}$	$4.4 \cdot 10^{-2}$	$1.9 \cdot 10^{-1}$

Case 3: (Hydroxyacetone hydrogenation to 1,2-propanediol is two-step irreversible reaction).

The overall reactions that describe the four reaction steps along with the resulting four rate equations are presented in Table S4. The results of the model are presented in Figure S6 as outlet concentration – time curves while in Table S5 are tabulated the values of all kinetic parameters, equilibrium and adsorption coefficients at 523K. The residual sum of squares in case 2 was 0.31.

Table S4: Elementary reactions and rate equations (Case 3)

	Elementary reactions	Rate equations

1st step - H ₂ formation	$\begin{aligned} \text{H}_2\text{O} + * &\leftrightarrow \text{H}_2\text{O}^* \\ \text{H}_2\text{O}^* + * &\leftrightarrow \text{OH}^* + \text{H}^* \\ \text{CH}_3\text{OH} + * &\leftrightarrow \text{CH}_3\text{OH}^* \\ \text{CH}_3\text{OH}^* + * &\rightarrow \text{CH}_3\text{O}^* + \text{H}^* \quad \text{RDS}_1 \\ &: \\ \text{CO}^* + \text{OH}^* &\rightarrow \text{H}^* + \text{CO}_2 \\ 2\text{H}^* &\leftrightarrow \text{H}_2 + 2* \end{aligned}$	$r_1 = k_1 \frac{K_{\text{CH}_3\text{OH}} C_{\text{CH}_3\text{OH}}}{(\text{DEN})^2}$
2nd step - Hydroxyacetone formation	$\begin{aligned} \text{G} + * &\leftrightarrow \text{G}^* \\ \text{G}^* + * &\rightarrow \text{HA}^* + \text{H}_2\text{O}^* \quad \text{RDS}_2 \\ \text{HA}^* &\leftrightarrow \text{HA} + * \end{aligned}$	$r_2 = k_2 \frac{K_G C_G}{(\text{DEN})^2}$
3rd step - 1,2-propanediol formation	$\begin{aligned} \text{HA}^* + \text{H}^* &\leftrightarrow \text{HAH}^* + * \\ \text{HAH}^* + \text{H}^* &\rightarrow \text{1,2-PDO}^* + * \quad \text{RDS}_3 \\ \text{1,2-PDO}^* &\leftrightarrow \text{1,2-PDO} + * \end{aligned}$	$r_3 = k_3 \frac{K_{\text{HAH}} K_{\text{HA}} C_{\text{HA}} K_{\text{H}_2} C_{\text{H}_2}}{(\text{DEN})^2}$
4th step - ethylene glycol formation	$\begin{aligned} \text{G}^* + \text{H}^* &\rightarrow \text{GH}^* + * \quad \text{RDS}_4 \\ \text{GH}^* + \text{H}^* &\rightarrow \text{EG}^* + \text{CH}_3\text{OH}^* \\ \text{EG}^* &\leftrightarrow \text{EG} + * \end{aligned}$	$r_4 = k_4 \frac{K_G C_G (K_{\text{H}_2} C_{\text{H}_2})^{0.5}}{(\text{DEN})^2}$
* = active site, G = glycerol, 1,2-PDO = 1,2-propanediol, EG = ethylene glycol, HA = hydroxyacetone, H = hydrogen		

Where, $\text{DEN} = 1 + K_G C_G + K_{\text{CH}_3\text{OH}} C_{\text{CH}_3\text{OH}} + K_{\text{HA}} C_{\text{HA}} + K_{\text{PG}} C_{\text{PG}} + (K_{\text{H}_2} C_{\text{H}_2})^{0.5} + K_{\text{HAH}} K_{\text{HA}} C_{\text{HA}} (K_{\text{H}_2} C_{\text{H}_2})^{0.5}$

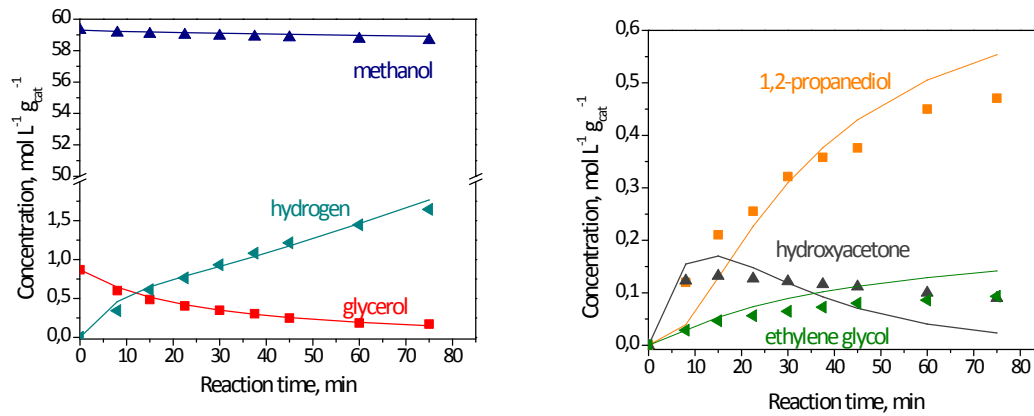


Figure S6: Experimental (points) and predicted (lines) values of reactants and products outlet concentrations as a function of reaction time (Case 3). Experimental conditions: aq. solution of 1wt% glycerol and 30wt% methanol, $m_{\text{glycerol}}/m_{\text{catalyst}} = 2.4$, 3.0MPa N₂, 523 K, 0-75min.

Table S5: Estimated values of kinetic parameters (Case3)

Kinetic	Step 1)	Step 2)	Step 3)	Step 4)
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parameters	Methanol APR	Glycerol dehydration	Hydroxyacetone hydrogenation	Glycerol hydrogenolysis
$k_i, \text{min}^{-1} (523\text{K})$	$9.6 \cdot 10^5$	$1.7 \cdot 10^7$	$2.6 \cdot 10^7$	$2.0 \cdot 10^7$

Adsorption coefficients					
	Methanol	Glycerol	1,2-propanediol	Hydroxyacetone	Hydrogen
$K_j, \text{g}_{\text{cat}} \cdot \text{L} \cdot \text{mol}^{-1} (523\text{K})$	$1.5 \cdot 10^{-4}$	$1.3 \cdot 10^{-3}$	1.0	$1.0 \cdot 10^{-2}$	$5.2 \cdot 10^{-2}$
Equilibrium coefficient					
Hydroxyacetone partial hydrogenation, K_{HAH}	8.1				

Case 4: (Hydroxyacetone hydrogenation to 1,2-propanediol is one-step reversible reaction). The overall reactions that describe the four reaction steps along with the resulting four rate equations are presented in Table S6. The results of the model are presented in Figure S7 as outlet concentration – time curves while in Table S7 are tabulated the values of all kinetic parameters, equilibrium and adsorption coefficients at 523K. The residual sum of squares in case 3 was 0.22.

Table S6: Elementary reactions and rate equations (Case 4)

	Elementary reactions	Rate equations
1st step - H ₂ formation	$\text{H}_2\text{O} + * \leftrightarrow \text{H}_2\text{O}^*$ $\text{H}_2\text{O}^* + * \leftrightarrow \text{OH}^* + \text{H}^*$ $\text{CH}_3\text{OH} + * \leftrightarrow \text{CH}_3\text{OH}^*$ $\text{CH}_3\text{OH}^* + * \rightarrow \text{CH}_3\text{O}^* + \text{H}^* \quad \text{RDS}_1$: $\text{CO}^* + \text{OH}^* \rightarrow \text{H}^* + \text{CO}_2$ $2\text{H}^* \leftrightarrow \text{H}_2 + 2^*$	$r_1 = k_1 \frac{K_{\text{CH}_3\text{OH}} C_{\text{CH}_3\text{OH}}}{(\text{DEN})^2}$
2nd step - Hydroxyacetone formation	$\text{G} + * \leftrightarrow \text{G}^*$ $\text{G}^* + * \rightarrow \text{HA}^* + \text{H}_2\text{O}^* \quad \text{RDS}_2$ $\text{HA}^* \leftrightarrow \text{HA} + *$	$r_2 = k_2 \frac{K_G C_G}{(\text{DEN})^2}$
3rd step - 1,2-propanediol formation	$\text{HA}^* + 2\text{H}^* \leftrightarrow 1,2\text{-PDO}^* + 2^* \quad \text{RDS}_3$ $1,2\text{-PDO}^* \leftrightarrow 1,2\text{-PDO} + *$	$r_3 = k_3 \frac{(K_{\text{HA}} C_{\text{HA}} K_{\text{H}_2} C_{\text{H}_2} - K_{\text{PG}} C_{\text{PG}} K_3^{-1})}{(\text{DEN})^3}$
4th step - ethylene glycol formation	$\text{G}^* + \text{H}^* \rightarrow \text{GH}^* + *$ $\text{GH}^* + \text{H}^* \rightarrow \text{EG}^* + \text{CH}_3\text{OH}^*$	$r_4 = k_4 \frac{K_G C_G (K_{\text{H}_2} C_{\text{H}_2})^{0.5}}{(\text{DEN})^2}$

EG* ↔ EG + *
*=active site, G=glycerol, 1,2-PDO=1,2-propanediol, EG=ethylene glycol, HA=hydroxyacetone, H =hydrogen

Where, $DEN = 1 + K_G C_G + K_{CH_3OH} C_{CH_3OH} + K_{HA} C_{HA} + K_{PG} C_{PG} + (K_{H_2} C_{H_2})^{0.5}$

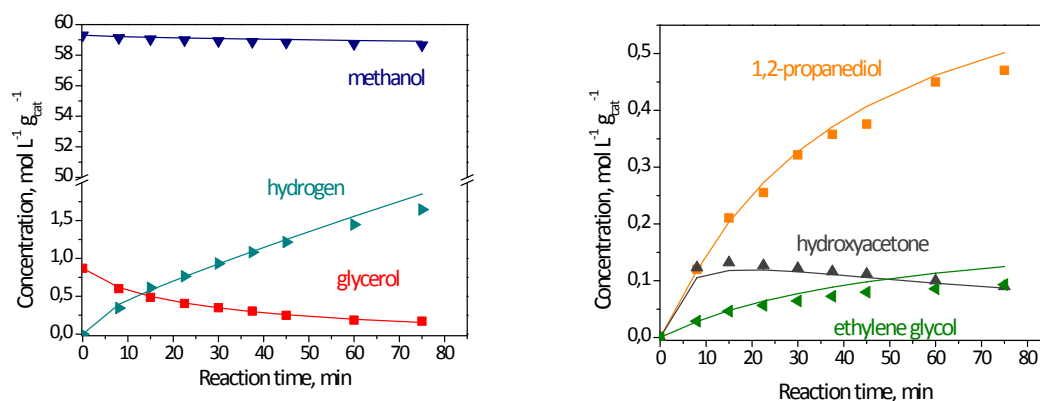


Figure S7: Experimental (points) and predicted (lines) values of reactants and products outlet concentrations as a function of reaction time (Case 4). Experimental conditions: aq. solution of 1wt% glycerol and 30wt% methanol, $m_{\text{glycerol}}/m_{\text{catalyst}} = 2.4$, 3.0MPa N_2 , 523 K, 0-75min.

Table S7: Estimated values of kinetic parameters (Case4)

Kinetic parameters	Step 1) Methanol APR	Step 2) Glycerol dehydration	Step 3) Hydroxyacetone hydrogenation	Step 4) Glycerol hydrogenolysis

$k_i, \text{min}^{-1} (523\text{K})$	$6.0 \cdot 10^5$	$3.7 \cdot 10^6$	$2.3 \cdot 10^{10}$	$1.1 \cdot 10^6$	
Adsorption coefficients					
	Methanol	Glycerol	1,2-propanediol	Hydroxyacetone	Hydrogen
$K_j, \text{g}_{\text{cat}} \cdot \text{L} \cdot \text{mol}^{-1} (523\text{K})$	$5.0 \cdot 10^{-4}$	$1.3 \cdot 10^{-2}$	$9.7 \cdot 10^{-1}$	$5.1 \cdot 10^{-1}$	$9.5 \cdot 10^{-1}$
Equilibrium coefficient					
1,2-propanediol formation, K_3	6.3				

Case 5: (Hydroxyacetone hydrogenation to 1,2-propanediol is two-step reversible reaction). The overall reactions that describe the four reaction steps along with the resulting four rate equations are presented in Table S8. The results of the model are presented in Figure S8 as outlet concentration – time curves while in Table S9 are tabulated the values of all kinetic parameters, equilibrium and adsorption coefficients at 523K. The residual sum of squares in case 3 was 0.22.

Table S8: Elementary reactions and rate equations (Case 5)

	Elementary reactions	Rate equations
1st step - H ₂ formation	$\text{H}_2\text{O} + * \leftrightarrow \text{H}_2\text{O}^*$ $\text{H}_2\text{O}^* + * \leftrightarrow \text{OH}^* + \text{H}^*$ $\text{CH}_3\text{OH} + * \leftrightarrow \text{CH}_3\text{OH}^*$ $\text{CH}_3\text{OH}^* + * \rightarrow \text{CH}_3\text{O}^* + \text{H}^* \quad \text{RDS}_1$: $\text{CO}^* + \text{OH}^* \rightarrow \text{H}^* + \text{CO}_2$ $2\text{H}^* \leftrightarrow \text{H}_2 + 2^*$	$r_1 = k_1 \frac{K_{\text{CH}_3\text{OH}} C_{\text{CH}_3\text{OH}}}{(\text{DEN})^2}$
2nd step - Hydroxyacetone formation	$\text{G} + * \leftrightarrow \text{G}^*$ $\text{G}^* + * \rightarrow \text{HA}^* + \text{H}_2\text{O}^* \quad \text{RDS}_2$ $\text{HA}^* \leftrightarrow \text{HA} + *$	$r_2 = k_2 \frac{K_G C_G}{(\text{DEN})^2}$
3rd step – 1,2-propanediol formation	$\text{HA}^* + \text{H}^* \leftrightarrow \text{HAH}^* + *$ RDS_3 $\text{HAH}^* + \text{H}^* \leftrightarrow 1,2\text{-PDO}^* + *$ $1,2\text{-PDO}^* \leftrightarrow 1,2\text{-PDO} + *$	$r_3 = k_3 \frac{(K_{\text{H}_2} C_{\text{H}_2})^{-0.5} (K_{\text{HA}} C_{\text{HA}} K_{\text{H}_2} C_{\text{H}_2} - (K_{\text{PG}} C_{\text{PG}} (K_3 K_{\text{HA}}))}{(\text{DEN})^2}$

4 th step – ethylene glycol formation	$G^* + H^* \rightarrow GH^* + *$ $GH^* + H^* \rightarrow EG^* + CH_3OH^*$ $EG^* \leftrightarrow EG + *$	RDS_4	$r_4 = k_4 \frac{K_G C_G (K_{H_2} C_{H_2})^{0.5}}{(DEN)^2}$
*=active site, G=glycerol, 1,2-PDO=1,2-propanediol, EG=ethylene glycol, HA=hydroxyacetone, H =hydrogen			

Where,

$$DEN = 1 + K_G C_G + K_{CH_3OH} C_{CH_3OH} + K_{HA} C_{HA} + K_{PG} C_{PG} + (K_{H_2} C_{H_2})^{0.5} + K_{PG} C_{PG} K_{HAH}^{-1} (K_{H_2} C_{H_2})^{-0.5}$$

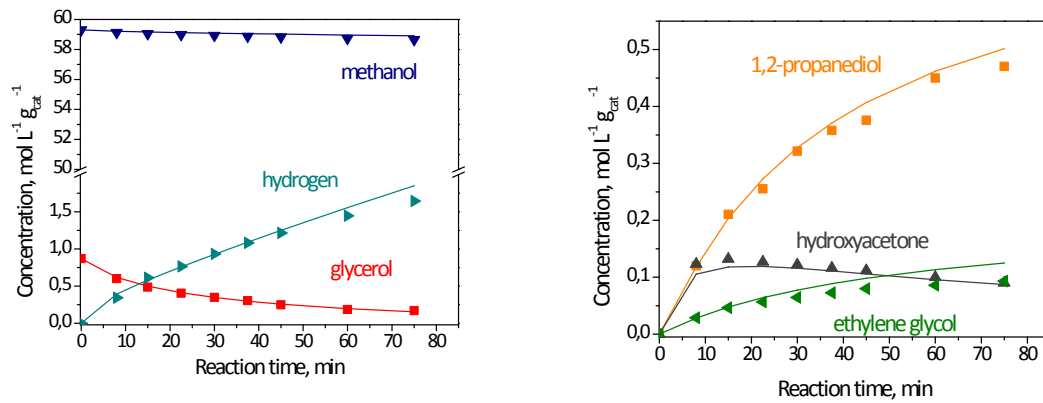


Figure S8: Experimental (points) and predicted (lines) values of reactants and products outlet concentrations as a function of reaction time (Case 5). Experimental conditions: aq. solution of 1wt% glycerol and 30wt% methanol, $m_{\text{glycerol}}/m_{\text{catalyst}} = 2.4$, 3.0MPa N_2 , 523 K, 0-75min.

Table S9: Estimated values of kinetic parameters (Case5)

Kinetic parameters	Step 1) Methanol APR	Step 2) Glycerol dehydration	Step 3) Hydroxyacetone hydrogenation	Step 4) Glycerol hydrogenolysis
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$k_i, \text{min}^{-1} (523\text{K})$	$3.1 \cdot 10^5$	$1.5 \cdot 10^6$	$8.4 \cdot 10^8$	$3.8 \cdot 10^6$
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Adsorption coefficients					
	Methanol	Glycerol	1,2-propanediol	Hydroxyacetone	Hydrogen
$K_j, \text{g}_{\text{cat}} \cdot \text{L} \cdot \text{mol}^{-1} (523\text{K})$	$1.4 \cdot 10^{-3}$	$4.9 \cdot 10^{-2}$	$1.1 \cdot 10^{-1}$	9.9	$7.2 \cdot 10^{-3}$
Equilibrium coefficient					
1,2-propanediol formation, K_3	2.9				