

Supplementary Information for
**Kinetic and Process Modeling of Guerbet Coupling
Chemistry over Cu-Mg-Al Mixed Oxides**

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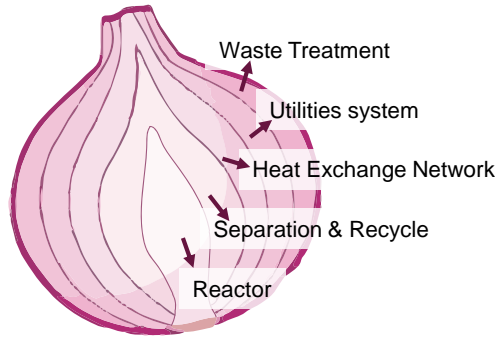
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Index

1	Process design hierarchy	S2
2	Development of kinetic model	S2
3	Transport Limitation Calculations	S4
4	Comparison of Experimental vs. Modeled Trends	S5
5	References	S8

S1. Process design hierarchy



Scheme S1. Hierarchical description of process design by the onion diagram. The inner shell of the onion represents the stage with the highest priority.¹

S2. Development of kinetic model

The mole balance equation for the species i participating in j reactions inside a flow reactor is given by equation (S1).

$$\frac{dF_i}{dV} = \sum_j \nu_{i,j} r'_j \quad (\text{S1})$$

The volume of the reactor can be rewritten as $V = w_{\text{cat}}/\rho_{\text{cat}}$, which can be introduced in equation (S1) to yield the expression for a packed-bed reactor as presented in equation (S2).

$$\frac{dF_i}{dw_{\text{cat}}} = \frac{1}{\rho_{\text{cat}}} \sum_j \nu_{i,j} r'_j \quad (\text{S2})$$

Where F_i represents the mole flow of species i , w_{cat} is the mass of the catalyst, ρ_{cat} is the bulk density of the catalyst, $\nu_{i,j}$ is the stoichiometric coefficient of species i in reaction j , and r'_j represents the reaction rate expression for reaction j . Multiplying both sides of equation (S2) by the mole flow in the inlet of the reactor (F_T^0) and replacing the term $\tau = \frac{w_{\text{cat}}}{F_T^0}$ we obtain

$$F_T^0 \frac{dF_i}{dw_{\text{cat}}} = \frac{dF_i}{d\left(\frac{w_{\text{cat}}}{F_T^0}\right)} = \frac{dF_i}{d\tau} = F_T^0 \sum_j \nu_{i,j} r'_j \quad (\text{S3})$$

Where $\rho_{\text{cat}} r_j = r'_j$. A set of ordinary differential equations is then created after applying equation (S3) to all the species generated/consumed during the reaction. In our model, for a generic reaction $aA + bB \rightleftharpoons cC + dD$ the rate of reaction j has been written in terms of an equilibrium-limited reaction as described in equation (S4).

$$r_j = k'_{f,j} \frac{\left(a_A^a a_B^b - \frac{a_C^c a_D^d}{K_{\text{eq},j}}\right)}{\left(1 + \sum_i K'_{\text{ads},i} a_i\right)^{a+b}} \quad (\text{S4})$$

The activity of species i in the gas phase is defined as $a_i = \frac{\phi_i P y_i}{f^\circ}$ and for simplicity we have assumed ideal gas behavior, which yields $\phi_i = 1 \forall i$. P and f° represent the pressure of the system and fugacity of an ideal gas at 1 bar. As regarded, we have adopted a LHHW adsorption expression to model our kinetics. In our expression $k'_{f,j}$ represents the forward kinetic rate constant of reaction j and $K'_{\text{ads},i}$ is the adsorption constant of species i . After replacing the expression for activity in equation (S4), we obtained Equation (S5).

$$r_j = k'_{f,j} \left(\frac{P}{f^\circ} \right)^{a+b} \frac{\left(y_A^a y_B^b - \frac{y_C^c y_D^d}{K_{\text{eq},j}} \left(\frac{P}{f^\circ} \right)^{\Delta n_j} \right)}{\left(1 + \sum_i K'_{\text{ads},i} \left(\frac{P}{f^\circ} \right) y_i \right)^{a+b}} \quad (\text{S5})$$

Where $\Delta n_j = \sum_i \nu_{i,j}$. After grouping $K_{\text{ads}} = K'_{\text{ads}} \left(\frac{P}{f^\circ} \right)$ and $k_{f,j} = k'_{f,j} \left(\frac{P}{f^\circ} \right)^{a+b}$, we obtain:

$$\frac{dF_i}{d\tau} = F_T^0 \sum_j \nu_{i,j} k_{f,j} \frac{\left(y_A^a y_B^b - \frac{y_C^c y_D^d}{K_{\text{eq},j}} \left(\frac{P}{f^\circ} \right)^{\Delta n_j} \right)}{\left(1 + \sum_i K_{\text{ads},i} y_i \right)^{a+b}} \quad (\text{S6})$$

As observed, the model solves the flow rate of species i in terms of mole fractions in the gas phase. Thereby, Equation (S6) needs to be solved simultaneously with Equation (S7), forming a differential-algebraic system of equations.

$$y_i = \frac{F_i}{\sum_j F_j} \quad (\text{S7})$$

From our experiments, we have collected liquid phase information, which demands the conversion of gas phase mole fractions from the model into liquid phase concentrations. First, liquid phase mole fractions need to be computed with information of condensable compounds by calculating a new set of mole fractions in hydrogen and carbon monoxide-free basis as presented in Equation (S8).

$$x_i = \frac{F_{i \neq (\text{CO}, \text{H}_2)}}{F_T - F_{\text{CO}} - F_{\text{H}_2}} = \frac{y_{i \neq (\text{CO}, \text{H}_2)}}{1 - y_{\text{CO}} - y_{\text{H}_2}} \quad (\text{S8})$$

Liquid phase concentrations are then calculated by using Equation (S9).

$$C_i = \frac{x_i}{\sum_i x_i \left(\frac{\text{MW}_i}{\rho_i} \right)} \quad (\text{S9})$$

Where C_i is the liquid phase concentration of species i in the mixture of products, MW_i is the molecular weight of species i , and ρ_i is the liquid phase density of species i at 20 °C.

S3. Transport Limitation Calculations

1. **Internal diffusion limitations:** Weisz-Prater criterion is defined in Equation S10.

$$C_w = \frac{r_0 \rho_{\text{cat}} R_p^2}{D_{\text{eff}} C_A} \quad (\text{S10})$$

- **Initial ethanol consumption rate** r_0 : For calculation of the initial reaction rate, we used Equation S11, which describes the change in ethanol flow as a function of the contact time.

$$\frac{dF_E}{d\tau} = F_T^0 \sum_j \nu_{E,j} r_j = F_T^0 r_0 \quad (\text{S11})$$

Introducing the ethanol conversion ($F_E^0 - F_E = F_E^0 x_E$) in Equation S11 yields equation S12.

$$-F_E^0 \left(\frac{dx_E}{d\tau} \right) = F_T^0 r_0 \quad (\text{S12})$$

Rearranging the Equation S12, and using the experimental values we obtain:

$$r_0 = \frac{F_E^0}{F_T^0} \left(\frac{dx_E}{d\tau} \right)_{\tau=0} = \frac{4}{5} \cdot 0.17 \frac{\text{kmol}_{\text{gas}}}{\text{h} \cdot \text{kg}_{\text{cat}}} = 0.0302 \frac{\text{mol}_{\text{Ethanol}}}{\text{s} \cdot \text{kg}_{\text{cat}}} \quad (\text{S13})$$

- **Catalyst density** ρ_{cat} : 3680 kg_{cat}m⁻³
- **Effective radius** R_p^2 : Before packing the catalyst, it was meshed with standard meshes and the fraction between 30-80 mesh was employed for the experiments. The opening size for the mesh 30 is 5.95E-4 m, which yield an effective radius of 2.975E-4 m.
- **Effective diffusivity coefficient** D_{eff} : The molecular theory was employed to estimate the diffusivity coefficient for the mixture H₂-ethanol at 325 °C and 21.4 bar. The calculated value is $D_{\text{H}_2\text{-Ethanol}} = 7.77\text{E-}6 \text{ m}^2 \text{ s}^{-1}$.²
- **Ethanol initial concentration** C_A :

$$C_{\text{Ethanol}} = \frac{P_{\text{Ethanol}}}{RT} = \frac{0.8 \cdot 21.4 \text{ atm}}{0.08206 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \cdot 598.15 \text{ K}} = 0.35 \text{ M} = 350 \frac{\text{mol}}{\text{m}^3} \quad (\text{S14})$$

The calculated Weisz-Prater number is $0.0036 \ll 1$, indicating that the reaction was kinetically controlled (internal diffusion limitations are negligible).

$$C_w = \frac{0.0302 \cdot 3680 \cdot (2.975\text{E-}4)^2}{7.77\text{E-}6 \cdot 350} = 0.0036 \quad (\text{S15})$$

2. **Internal heat transfer:** Prater number (β). The reaction that initiates the coupling chemistry is ethanol dehydrogenation into acetaldehyde. This reaction has a heat of reaction of 67655 J·mol⁻¹ at 325 °C. For the calculation, we have used the thermal conductivity of magnesia of 50 W·m⁻¹·K⁻¹. Also, the surface temperature of the catalyst (T_s) was assumed to be the reaction temperature. No important heat gradients are expected in the particles.

$$\beta = \frac{\Delta H_{\text{rxn}} r_A R_p^2}{\lambda T_s} = \frac{67655 \cdot 0.0302 \cdot 3680 \cdot (2.975\text{E-}4)^2}{50 \cdot 598.15} = 2.2\text{E-}5 \quad (\text{S16})$$

S4. Comparison of Experimental vs. Modeled Trends

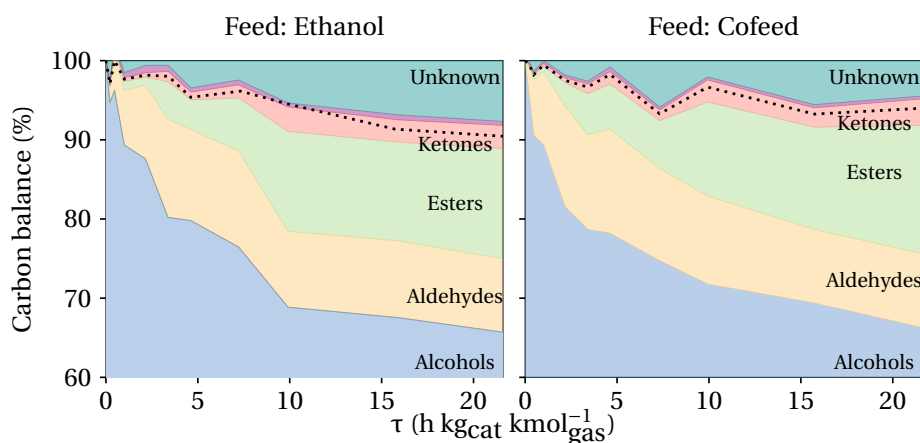


Figure S1: Carbon balance per groups as a function of time on stream (τ) for experiments with pure ethanol feed (left) and cofeed (right). The areas represent the carbon fraction that was identified in: ■ Alcohols, ■ Aldehydes, ■ Esters, ■ Ketones, ■ Paraffins + olefins + ethers, and ■ Unknown. Dotted line represents the carbon balance that can be explained by the species employed to build the kinetic model.

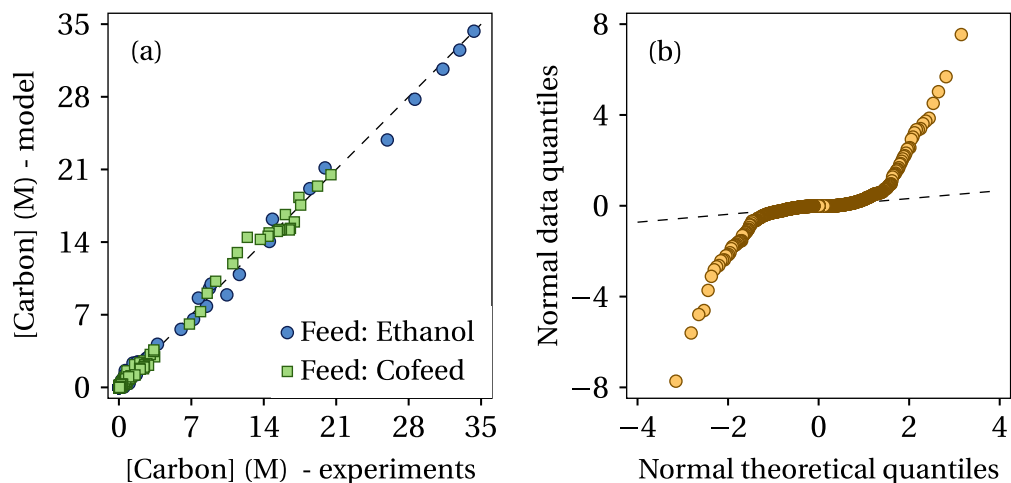


Figure S2: (a) Parity plot of the carbon concentration predicted by the model vs. the experimental carbon concentration fed to the optimization algorithm. (b) Quantile-quantile plot of the residuals of the model.

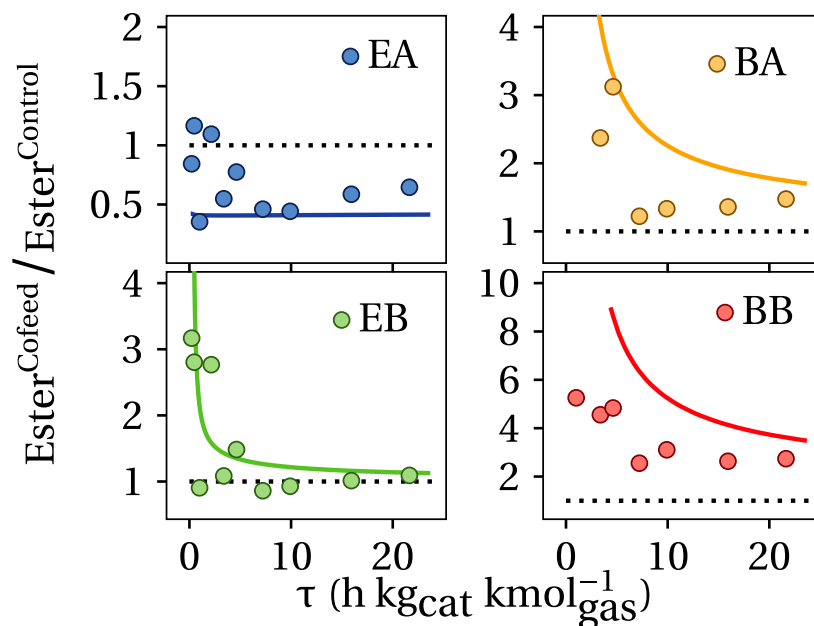


Figure S3: Relative concentration ratio of alcohols in cofeed to control (pure ethanol feed) experiments. Reaction conditions: 325°C, 300 psig, (Ethanol + Butanol)/H₂=4, catalyst: Cu_{0.01}Mg_{2.99}AlO. Cofeed: ethanol-butanol 70-30% mole basis. Solid lines represent the prediction of the model. Dotted line at ratio=1 has been added as visual aid. EA: Ethyl acetate, BA: Butyl acetate, EB: Ethyl butyrate, BB: Butyl butyrate.

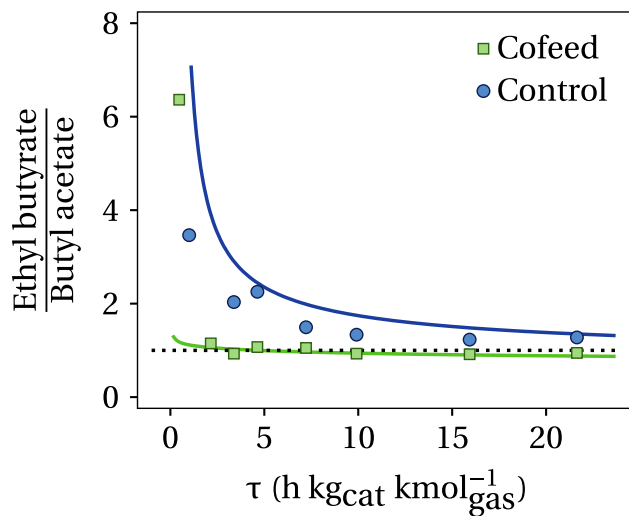


Figure S4: Relative concentration ratio of ethyl butyrate to butyl acetate for cofeed and pure ethanol (control) experiments. Reaction conditions: 325°C, 300 psig, (Ethanol + Butanol)/H₂ = 4, catalyst: Cu_{0.01}Mg_{2.99}AlO. Cofeed: ethanol-butanol 70-30% mole basis. Solid lines represent the prediction of the model. Dotted line at ratio=1 has been added as visual aid.

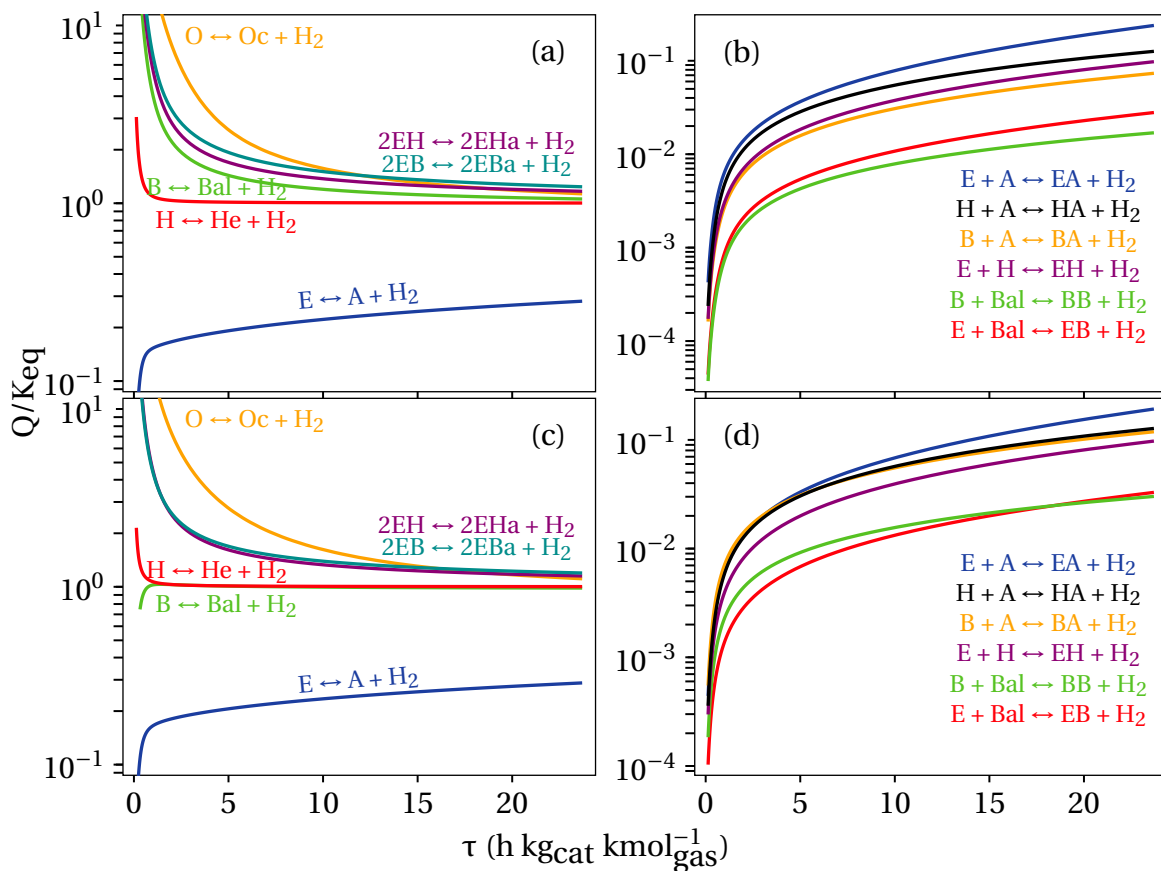


Figure S5: Relative position of the equilibrium reactions as a function of the contact time for the control (a and b) and cofeed (c and d) experiments. E: Ethanol, A: Acetaldehyde, B: Butanol, Bal: Butyraldehyde, H: Hexanol, He: Hexanal, O: Octanol, Oc: Octanal, 2EB: 2-Ethylbutanol, 2EBa: 2-Ethylbutanal, 2EH: 2-Ethylhexanol, 2EHa: 2-Ethylhexanal, EA: Ethyl acetate, EB: Ethyl butyrate, BA: Butyl acetate, BB: Butyl butyrate, HA: Hexyl acetate, and EH: Ethyl hexanoate.

Table S1: Set of equilibrium reactions implemented in the Aspen Plus simulation for the hydrogenolysis reactor.

Reaction Number	Reaction
1	acetaldehyde + H ₂ → ethanol
2	butyraldehyde + H ₂ → butanol
3	hexanal + H ₂ → hexanol
4	2-ethyl-1-butanol + H ₂ → 2-ethyl-1-butanol
5	2-ethyl-1-hexanal + H ₂ → 2-ethyl-1-hexanol
6	octanal + H ₂ → octanol
7	decanal + H ₂ → decanol
8	acetone + H ₂ → isopropyl alcohol
9	2-butanone + H ₂ → 2-butanol
10	2-pentanone + H ₂ → 2-methyl-1-butanol
11	2-heptanone + H ₂ → 2-heptanol
12	2-octanone + H ₂ → 2-octanol
13	2-nonanone + H ₂ → 2-nonanol
14	2-undecanone + H ₂ → 2-undecanol
15	ethyl acetate + 2 H ₂ → 2 ethanol
16	ethyl butyrate + 2 H ₂ → ethanol + butanol
17	butyl acetate + 2 H ₂ → ethanol + butanol
18	butyl butyrate + 2 H ₂ → 2 butanol
19	ethyl hexanoate + 2 H ₂ → ethanol + hexanol
20	hexyl acetate + 2 H ₂ → ethanol + hexanol
21	butyl hexanoate + 2 H ₂ → butanol + hexanol
22	hexyl butyrate + 2 H ₂ → butanol + hexanol
23	hexyl hexanoate + 2 H ₂ → 2 hexanol
24	butyl octanoate + 2 H ₂ → butanol + octanol
25	butyl decanoate + 2 H ₂ → butanol + decanol

S5. References

- (1) R. Smith and B. Linnhoff, *Chem. Eng. Res. Des.:(United Kingdom)*, 1988, **66**.
- (2) B. E. Poling, J. M. Prausnitz and J. P. O'Connell, *Properties of Gases and Liquids*, McGraw-Hill Education, New York, 5th Edition edn., 2001.