An elementary-step kinetic model for ethyl acetate synthesis by direct addition of acetic acid to ethylene on a silicotungstic acid catalyst. – Supporting Information

SI 1. Adsorption entropies and pre-exponential factors

The adsorption entropies and pre-exponential factors of the Langmuir-Hinshelwood-Hougen-Watson (LHHW) model (Section SI 3), solvation and clustering LHHW and solvation and clustering LHHWER (combined Langmuir-Hinshelwood-Hougen-Watson and Eley-Rideal) are determined based on the order of magnitude data as reported by Dumesic [1]. The adsorption entropies can be determined by considering the nature of the adsorbate transition state and comparing the rotational and translational freedom between adsorbate and adsorption transition state. For all species, an immobile adsorption state was assumed for adsorption, which results in an adsorption pre-exponential factor equal to 10^6 MPa^{-1} s^{-1}. For desorption, similar freedom for adsorbate and transition state for ethylene (C_2H_4) and more freedom for the adsorption transition state of the other species was assumed, which leads to desorption pre-exponential factors equal to 10^{13} s^{-1} for C_2H_4 and 10^{16} s^{-1} for H_2O and the oxygenates. During the kinetic model development, these assumption lead to the best regression results in terms of parameter estimates (adsorption enthalpies) and model predictions. By calculating the ratio of adsorption and desorption, the adsorption entropies as reported in Table 1, SI 3 and SI 4 can be determined.

Dumesic’s data as well as the proton concentration per unit volume of catalyst have also been used to determine the pre-exponential factors of the reactions. In case of the LHHW and solvation and clustering LHHW model, for the reactions involving C_2H_4, i.e. r_1, r_2 and r_3 (Scheme 1) immobile surface species without rotation were assumed, which results in pre-exponential factors equal to 10^{11} s^{-1} per active site. For reactions r_4 and r_5, which are likely to proceed in the pseudo-liquid phase of the catalyst, mobile surface species with rotation was assumed, for which the pre-exponential factors amount to 10^8 s^{-1} per active site. For the solvation and clustering LHHWER model, immobile surface species without rotation was assumed for r_1 and r_2 (LHHW type reactions) and an immobile transition state for r_3 (ER type reaction). Hence, the pre-exponential factors of r_1 and r_2 are equal to 10^{11} s^{-1} per active site, while the factor for r_3 amounts to 10^7 MPa^{-1} s^{-1} per active site. For r_4 (LHHW type reaction) and r_5 (ER type reaction) mobile surface species with rotation and a mobile transition state were supposed respectively, for which the pre-exponential factors are 10^8 s^{-1} per active site and 10^9 MPa s^{-1} per active site respectively. These assumptions were used to determine the pre-exponential factors as listed in Table 1, SI 3 and SI 4, and lead to the best model performance, considering the parameter estimates and model predictions.

SI 2. Power law kinetic model

The rate equations (r_l) of the power law kinetic model are presented by Eq. (SI 1) and include reaction rate coefficients (k_l, mol m^{-3} MPa$^{-(2+\alpha+\beta+\gamma)}$ s^{-1}), driving force terms and the fugacities of ethylene (f_{C2H4}, MPa), acetic acid (AcOH, f_{AcOH}, MPa) and water (H_2O, f_{H2O}, MPa) powered to exponents α, β and γ respectively. The reaction rate coefficients are evaluated by the reparametrized Arrhenius relationship (Eq. (SI 2)) for which both the pre-exponential factor (A_l, mol m^{-3} MPa$^{-(2+\alpha+\beta+\gamma)}$ s^{-1}) and activation energy ($E_{a,l}$, kJ mol^{-1}) are determined by regression. The driving force term is included, because reverse reactions are important for experiments during which products are present in the feed. As with the solvation and clustering LHHWER model, the overall reaction equilibrium coefficients ($K_{eq,l}$, - or MPa) is determined via ASPEN and NIST data [2, 3]. To minimize the number of parameters, the f_{C2H4}, f_{AcOH} and f_{H2O} are powered to the same exponents $\alpha_{1\text{-}3}$, $\beta_{1\text{-}3}$ and $\gamma_{1\text{-}3}$ respectively for r_1 to r_3, given the assumption that the direct addition rates are similarly affected by the fugacities of the reactants. The fugacities of products, i.e. ethyl acetate (EtOAc, f_{EtOAc}, MPa), ethanol (EtOH, f_{EtOH}, MPa) and diethyl ether (DEE, f_{DEE}, MPa), powered to an exponent are not included in the rate equations, because the model regression leads to negative exponents, resulting in divisions by zero during calculations of reaction rates when the fugacities of products are 0 MPa, e.g. at the inlet of the reactor when no products are present in the feed.

$$\begin{cases} r_1 = k_1\left(f_{C_2H_4} f_{AcOH} - K_{eq,1}^{-1} f_{EtOAc}\right) f_{C_2H_4}^{\alpha_{1-3}} f_{AcOH}^{\beta_{1-3}} f_{H_2O}^{\gamma_{1-3}} \\ r_2 = k_2\left(f_{C_2H_4} f_{H_2O} - K_{eq,2}^{-1} f_{EtOH}\right) f_{C_2H_4}^{\alpha_{1-3}} f_{AcOH}^{\beta_{1-3}} f_{H_2O}^{\gamma_{1-3}} \\ r_3 = k_3\left(f_{C_2H_4} f_{EtOH} - K_{eq,3}^{-1} f_{DEE}\right) f_{C_2H_4}^{\alpha_{1-3}} f_{AcOH}^{\beta_{1-3}} f_{H_2O}^{\gamma_{1-3}} \\ r_4 = k_4\left(f_{AcOH} f_{EtOH} - K_{eq,4}^{-1} f_{H_2O} f_{EtOAc}\right) f_{C_2H_4}^{\alpha_4} f_{AcOH}^{\beta_4} f_{H_2O}^{\gamma_4} \\ r_5 = k_5\left(f_{EtOH}^2 - K_{eq,5}^{-1} f_{H_2O} f_{DEE}\right) f_{C_2H_4}^{\alpha_5} f_{AcOH}^{\beta_5} f_{H_2O}^{\gamma_5} \end{cases} \quad \text{(SI 1)}$$

$$k_l = A_l^{rep} \exp\left(-\frac{E_{a,l}}{R}\left(\frac{1}{T} - \frac{1}{T_{av}}\right)\right) \quad \text{(SI 2)}$$

Table SI 1 presents the parameter regression results for the power law model. The pre-exponential factors of r_1 and r_3 are negative, which are therefore not physically meaningful, hence the parameters were re-estimated while excluding r_1 and r_3 for which the results can be consulted in Table SI 2. The estimated exponents are mostly negative and vary between -4.2 to -1.3 for γ. Moreover, the power law model predicts stronger dependences for f_{H2O} compared to LHHW or ER type kinetic models. The fugacity dependences of LHHW and ER type models are minimum -2 or -1 respectively, due to the exponent of the adsorption term in the denominator of the rate equations. Hence, LHHW and ER type rate equations should be adjusted to enhance model performance.

Table SI 1: Parameter regression results of the power law model and corresponding 95% confidence intervals.

Rate coefficient	**A^{rep}/A^{rep}_{max} (-)**			**E_a (kJ mol^{-1})**		
k_1	$-3.2\cdot10^{-7}$	±	$5.2\cdot10^{-8}$	68.6	±	9.2
k_2	$6.7\cdot10^{-7}$	±	$9.0\cdot10^{-8}$	130.3	±	2.5
k_3	$-9.3\cdot10^{-8}$	±	$2.2\cdot10^{-7}$	-159.4	±	486.8
k_4	$8.0\cdot10^{-1}$	±	$6.2\cdot10^{-1}$	-29.7	±	6.5
k_5	$6.7\cdot10^{-1}$	±	1.0	69.8	±	30.5
Exponent	**Value (-)**					
α_{1-3}	$1.2\cdot10^{-1}$	±	$5.2\cdot10^{-2}$			
α_4	-1.1	±	$3.1\cdot10^{-1}$			
α_5	-1.4	±	$6.0\cdot10^{-1}$			
β_{1-3}	$4.4\cdot10^{-1}$	±	$9.2\cdot10^{-2}$			
β_4	1.4	±	$2.1\cdot10^{-1}$			
β_5	1.9	±	$3.0\cdot10^{-1}$			
γ_{1-3}	-2.9	±	$1.0\cdot10^{-1}$			
γ_4	-2.1	±	$2.7\cdot10^{-1}$			
γ_5	-2.3	±	$4.7\cdot10^{-1}$			

Table SI 2: Parameter regression results of the re-estimated power law model excluding r_1 and r_3 and corresponding 95% confidence intervals.

Rate coefficient	**A^{rep}/A^{rep}_{max} (-)**			**E_a (kJ mol^{-1})**		
k_1						
k_2	$1.7\cdot10^{-6}$	±	$2.9\cdot10^{-7}$	157.8	±	1.5
k_3						
k_4	$4.4\cdot10^{-1}$	±	$4.1\cdot10^{-1}$	-3.5	±	6.4
k_5	1.0	±	$4.3\cdot10^{-1}$	193.9	±	28.4
Exponent	**Value (-)**					
α_{1-3}	$-1.0\cdot10^{-1}$	±	$6.2\cdot10^{-2}$			
α_4	$-8.2\cdot10^{-1}$	±	$3.6\cdot10^{-1}$			
α_5	-2.2	±	$7.0\cdot10^{-1}$			
β_{1-3}	$1.2\cdot10^{-1}$	±	$6.1\cdot10^{-2}$			
β_4	$3.4\cdot10^{-1}$	±	$2.8\cdot10^{-1}$			
B_5	3.5	±	$3.5\cdot10^{-1}$			
γ_{1-3}	-2.3	±	$4.3\cdot10^{-2}$			
γ_4	-1.3	±	$2.5\cdot10^{-1}$			
γ_5	-4.2	±	$6.6\cdot10^{-1}$			

SI 3. Langmuir-Hinshelwood-Hougen-Watson kinetic model

The reaction rate equations of a LHHW kinetic model are given by Eq. (SI 3). The fractional coverages can be determined by Eq. (11), where the adsorption equilibrium constant is calculated by the Gibbs free energy of adsorption (Eq. (12)). The adsorption entropies are determined similarly according to the solvation and clustering LHHWER model and adsorption enthalpies are obtained by regression to experimental data (Section 2.3 to 2.5 and 3). For this model, the site balance includes the adsorption of DEE and is given by Eq. (SI 4).

$$\begin{cases} r_1 = k_1\left(\theta_{C_2H_4}\theta_{AcOH} - K_1^{-1}\theta_{EtOAc}\theta_*\right) \\ r_2 = k_2\left(\theta_{C_2H_4}\theta_{H_2O} - K_2^{-1}\theta_{EtOH}\theta_*\right) \\ r_3 = k_3\left(\theta_{C_2H_4}\theta_{EtOH} - K_3'^{-1}\theta_{DEE}\theta_*\right) \\ r_4 = k_4\left(\theta_{AcOH}\theta_{EtOH} - K_4^{-1}\theta_{H_2O}\theta_{EtOAc}\right) \\ r_5 = k_5\left(\theta_{EtOH}^2 - K_5'^{-1}\theta_{H_2O}\theta_{DEE}\right) \end{cases} \tag{SI 3}$$

$$\theta_* + \theta_{C_2H_4} + \theta_{AcOH} + \theta_{H_2O} + \theta_{EtOAc} + \theta_{EtOH} + \theta_{DEE} = 1 \tag{SI 4}$$

The reaction rate coefficients are evaluated according to the Arrhenius relationship (Eq. (14)), where the pre-exponential factors are set identically to the factors selected for the solvation and clustering LHHWER model and the activation energies are obtained by regression as well (Section 2.3). The surface reaction equilibrium coefficients ($K_{s,l}$) of r_1, r_2 and r_4 are function of the adsorption equilibrium coefficients ($K_{ads,j}$) and overall reaction equilibrium constants ($K_{eq,l}$) according to Eq. (27), (28) and (30) respectively. For r_3 and r_5 , the relationships between $K_{eq,l}$, $K_{s,l}$ and $K_{ads,l}$ are given by Eq. (SI 5) and (SI 6) respectively.

$$K_{eq,3} = \frac{K'_{s,3}K_{ads,C_2H_4}K_{ads,EtOH}}{K_{ads,DEE}} \tag{SI 5}$$

$$K_{eq,5} = \frac{K'_{s,5}K_{ads,EtOH}^2}{K_{ads,H_2O}K_{ads,DEE}} \tag{SI 6}$$

The regression results can be consulted in Table SI 3, where only the adsorption coefficient of DEE is regressed insignificantly. This might be rationalized by the lower concentration of DEE in the product compared to the other components. Moreover, only a few experiments with DEE present in the feed were conducted, during which the temperature was constant. Hence, the insignificant estimated adsorption enthalpy can be explained by the limited variation in the DEE adsorption with temperature. The high F value indicates that the model is globally significant. Given the much smaller adsorption enthalpy of DEE compared to the other components and identical adsorption entropy compared to water and the oxygenates, the adsorption coefficient of DEE is negligible compared to all other adsorption coefficients. Furthermore, within the experimental domain, its fugacity is in the same order of magnitude compared to EtOAc and EtOH, indicating that its contribution to the adsorption term in the reaction rates is negligible and is therefore be ignored in the solvation and clustering LHHW model and solvation and clustering LHHWER model.

Table SI 3: Parameter regression results of the solvation and clustering LHHWER model and corresponding 95% confidence intervals. The F value for the global significance of the regression equals equals $3.5 \cdot 10^7$ (tabulated value = 3.8) and R² amounts to 0.99999. The pre-exponential factors and adsorption entropies are set a priori.

Rate coefficient	**A/A_{max} (-)**	**E_a (kJ mol^{-1})**
k_1	1.0	36.0 ± 8.3
k_2	1.0	54.9 ± 5.6
k_3	1.0	35.7 ± 7.2
k_4	$1.0 \cdot 10^{-5}$	2.6 ± 1.6
k_5	$1.0 \cdot 10^{-5}$	15.4 ± 10.9

Adsorption coefficient	**$\Delta S_{ads}/\lvert\Delta S_{ads,max}\rvert$ (-)**	**ΔH_{ads} (kJ mol^{-1})**
K_{ads,C_2H_4}	$-6.7 \cdot 10^{-1}$	-115.8 ± 4.1
$K_{ads,AcOH}$	-1.0	-181.6 ± 6.2
K_{ads,H_2O}	-1.0	-205.1 ± 3.0
$K_{ads,EtOAc}$	-1.0	-198.4 ± 2.6
$K_{ads,EtOH}$	-1.0	-185.4 ± 6.2
$K_{ads,DEE}$	-1.0	-84.1

SI 4. Comparison of the power law and Langmuir-Hinshelwood-Hougen-Watson model

Figure SI 1 shows the effect of temperature (T) and total pressure (p_t) on AcOH conversion (x_{AcOH}) as function of relative space time ($(W/F^0)_{rel}$) and corresponding prediction by the power law and LHHW model. As can be seen, both models can accurately predict the increase in conversions with temperature, although at higher temperatures (T > 451 K) larger deviations between experimental data point and model prediction as well between two models are observed (See Figure SI 1 A). The power law model can accurately predict the decrease in AcOH conversion with total pressure, while simulations with the LHHW model do not capture the pressure effect (See Figure SI 1 B).

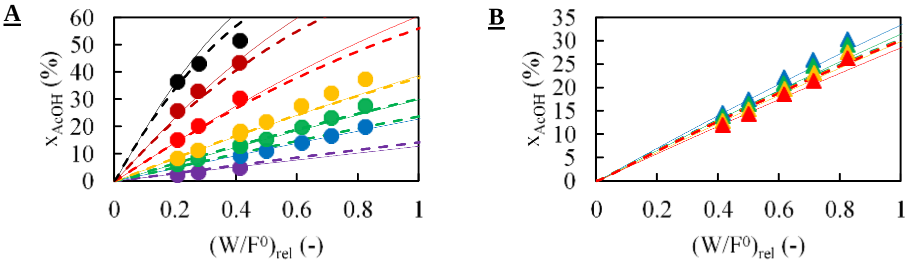

Figure SI 1: Effect of T (**A**) and p_t (**B**) on x_{AcOH} as function of $(W/F^0)_{rel}$ at (**A**) p_t = 1.2 MPa and the molar C_2H_4:AcOH:H_2O:N_2 feed ratio = 78.2:6.5:5.3:10.0, (**B**) T = 442 K and the molar C_2H_4:AcOH:H_2O:N_2 feed ratio = 78.2:6.5:5.3:10.0, (●) T = 433 K, (●) T = 439 K, (●) T = 442 K, (●) T = 445 K, (●) T = 451 K, (●) T = 457 K, (●) T = 463 K, (▲) p_t = 0.8 MPa, (▲) p_t = 1.0 MPa, (▲) p_t = 1.2 MPa and (▲) p_t = 1.4 MPa. Symbols represent experimental data points, the full and dashed lines are power law and LHHW model calculated values respectively.

SI 5. Solvation and clustering Langmuir-Hinshelwood-Hougen-Watson model

The solvation and clustering LHHW model is presented by the rate equations in Eq. (SI 7). As with the LHHW model (Section SI 3), the fractional coverages are determined according to Eq. (11). where the adsorption equilibrium coefficients are calculated by the Gibbs free energy of adsorption (Eq. (12). The adsorption entropies are identical to the entropies set for solvation and clustering LHHWER model and the adsorption enthalpies are determined by regression. For this model, the site balance (Eq. (SI 8)) excludes the adsorption of DEE.

$$\begin{cases} r_1 = k_1\varphi_a\varepsilon_{nc}\left(\theta_{C_2H_4}\theta_{AcOH} - K_1^{-1}\theta_{EtOAc}\theta_*\right) \\ r_2 = k_2\varphi_a\varepsilon_{nc}\left(\theta_{C_2H_4}\theta_{H_2O} - K_2^{-1}\theta_{EtOH}\theta_*\right) \\ r_3 = k_3\varphi_a\varepsilon_{nc}\left(\theta_{C_2H_4}\theta_{EtOH} - K_3'^{-1}\theta_* f_{DEE}\right) \\ r_4 = k_4\varphi_a\varepsilon_{nc}\left(\theta_{AcOH}\theta_{EtOH} - K_4^{-1}\theta_{H_2O}\theta_{EtOAc}\right) \\ r_5 = k_{5\varphi_a\varepsilon_{nc}}\left(\theta_{EtOH}^2 - K_5''^{-1}\theta_{H_2O}\theta_* f_{DEE}\right) \end{cases} \tag{SI 7}$$

$$\theta_* + \theta_{C_2H_4} + \theta_{AcOH} + \theta_{H_2O} + \theta_{EtOAc} + \theta_{EtOH} = 1 \tag{SI 8}$$

The reaction rate coefficient is evaluated according to the Arrhenius relationship (Eq. (14)), where the pre-exponential factor are set identically to the factors selected for the solvation and clustering LHHWER model and the activation energy is obtained by regression. The surface reaction equilibrium coefficients of r_1, r_2 and r_4 are function of the adsorption and overall reaction equilibrium coefficients according to Eq. (27), (28) and (30), the relationship between adsorption, surface and overall reaction equilibrium coefficients of r_3 and r_5 are given by Eq. (SI 5) and (SI 9) respectively.

$$K_{eq,5} = \frac{K_{s,5}''K_{ads,EtOH}^2}{K_{ads,H_2O}} \tag{SI 9}$$

The fractions of associated silicotungstic acid (STA) and non-clustered protons, i.e. φ_a and ε_{nc} respectively, are determined by Eq. (19) to (21) and (22) to (24) for which the corresponding enthalpy and entropy contributions are obtained by regression. The parameter regression results of the solvation and clustering LHHW model can be consulted in Table SI 4.

Table SI 4: Parameter regression results of the solvation and clustering LHHW model, corresponding 95% confidence intervals and t values (tabulated value = 2.0). The F value for the global significance of the regression equals $5.9 \cdot 10^8$ (tabulated value = 3.8) and R^2 is 0.99999. The pre-exponential factors and adsorption entropies are set a priori. Note that the t value and confidence interval of the corresponding parameter contain the same statistical information.

Rate coefficient	**A/A_{max} (-)**		**E_a (kJ mol^{-1})**	**t value (-)**
k_1	1.0		49.3 ± 7.3	13
k_2	1.0		51.3 ± 6.8	15
k_3	1.0		29.6 ± 7.3	8
k_4	$1.0 \cdot 10^{-5}$		21.7 ± 2.0	22
k_5	$1.0 \cdot 10^{-5}$		9.2	-
Adsorption coefficient	**$\Delta S_{ads}/\lvert\Delta S_{ads,max}\rvert$ (-)**		**ΔH_{ads} (kJ mol^{-1})**	**t value (-)**
K_{ads,C_2H_4}	$-6.7 \cdot 10^{-1}$		-110.8 ± 4.9	45
$K_{ads,AcOH}$	-1.0		-198.5 ± 5.5	71
K_{ads,H_2O}	-1.0		-199.7 ± 5.0	79
$K_{ads,EtOAc}$	-1.0		-194.3 ± 5.2	74
$K_{ads,EtOH}$	-1.0		-180.0 ± 4.9	72
STA solvation and proton-EtOH clustering coefficient	**$\Delta S_{solv/clus}$ (J mol^{-1} K^{-1})**	**t value (-)**	**$\Delta H_{solv/clus}$ (kJ mol^{-1})**	**t value (-)**
K_{solv}	-126.0 ± 13.1	-22	-65.4 ± 5.6	-23
K_{clus}	-106.5 ± 26.8	-9	-64.1 ± 11.8	-11

SI 6. Comparison of the solvation and clustering LHHWER and solvation and clustering LHHW model

Experiments have been performed with EtOH present in the feed, for which the feed fraction (y_{EtOH}^0) is varied between 0.0 and 2.0 mol%. Figure SI 2 shows the AcOH conversion as function of the relative space time and EtOH feed concentration and corresponding model predictions by the solvation and clustering LHHWER and solvation and clustering LHHW model. It is clearly observed that x_{AcOH} is only well predicted by the solvation and clustering LHHWER model when y_{EtOH}^0 exceeds 1.0 mol%.

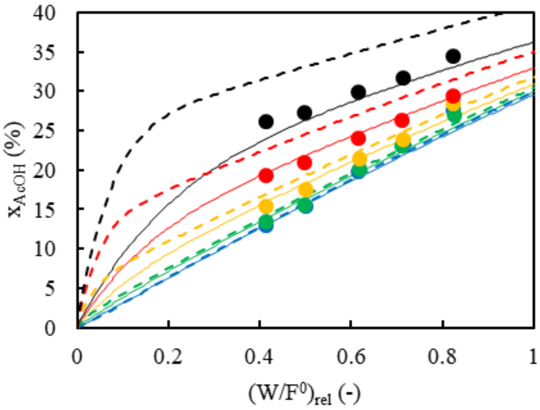

Figure SI 2: Effect of y_{EtOH}^0 on x_{AcOH} as function of $(W/F^0)_{rel}$ at (**A**) p_t = 1.2 MPa and $y_{C_2H_4}^0$ = 78.2 mol%, y_{AcOH}^0 = 6.5 mol% and $y_{H_2O}^0$ = 5.3 mol%, (●) y_{EtOH}^0 = 0.0 mol%, (●) y_{EtOH}^0 = 0.1 mol%, (●) y_{EtOH}^0 = 0.4 mol% K, (●) y_{EtOH}^0 = 1.0 mol% and (●) y_{EtOH}^0 = 2.0 mol%. Symbols represent experimental data points, the full and dashed lines are solvation and clustering LHHWER and solvation and clustering LHHW model calculated values respectively.

SI 7. References

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