

# UC Berkeley

## UC Berkeley Previously Published Works

### Title

Ethanol Conversion to Butadiene over Isolated Zinc and Yttrium Sites Grafted onto Dealuminated Beta Zeolite

### Permalink

<https://escholarship.org/uc/item/46g6g43p>

### Journal

Journal of the American Chemical Society, 142(34)

### ISSN

0002-7863

### Authors

Qi, Liang  
Zhang, Yanfei  
Conrad, Matthew A  
et al.

### Publication Date

2020-08-26

### DOI

10.1021/jacs.0c06906

Peer reviewed

## Supporting Information

### Ethanol Conversion to Butadiene over Isolated Zinc and Yttrium

#### Sites Grafted onto Dealuminated Beta Zeolite

Liang Qi<sup>1,2</sup>, Yanfei Zhang<sup>2</sup>, Matthew A. Conrad<sup>3</sup>, Christopher K. Russell<sup>3</sup>,  
Jeffrey Miller<sup>3</sup>, and Alexis T. Bell<sup>\*1,2</sup>

<sup>1</sup>Chemical Sciences Division  
Lawrence Berkeley National Laboratory  
Berkeley, CA 94720

<sup>2</sup>Department of Chemical and Biomolecular Engineering  
University of California  
Berkeley, CA 94720

<sup>3</sup>Davidson School of Chemical Engineering  
Purdue University  
West Lafayette, IN 47907

<b>Table of Contents</b>	<b>Page</b>
Figures S1-S5, S9, Table S1-S3: Supplemental catalyst characterization (BET, XRD, <sup>27</sup> Al NMR, ICP, FTIR-py, EXAFS, XANES)	S2-S5, S7
Figure S6: EtOH conversion over DeAlBEA catalyst	S5
Figure S7: AcH formation rate over 0.075Zn-DeAlBEA and 0.15Zn-DeAlBEA	S6
Figure S8. Comparison of 1,3-BD formation between 0.075Y-DeAlBEA and DeAlBEA catalysts.	S6
Figure S10. The observed ratio of consumed EtOH and AcH for 1,3-BD generation over 0.075Y-DeAlBEA.	S7
Figure S11. Evolution of 1,3-BD productivity and selectivity with TOS for 0.375Y-DeAlBEA and 0.15Zn-0.225Y-DeAlBEA	S8
Derivation of Rate Expressions	S9-S11

**Table S1. Microporous Surface Area for Different Samples**

Catalyst	Microporous surface area $\text{m}^2 \text{g}^{-1}$
H-BEA	370.4
DeAlBEA	352.6
0.075Zn-DeAlBEA	352.8
0.15Zn-DeAlBEA	353.5
0.375Zn-DeAlBEA	364.7
0.075Y-DeAlBEA	370.6
0.15Y-DeAlBEA	366.8
0.375Y-DeAlBEA	334.4

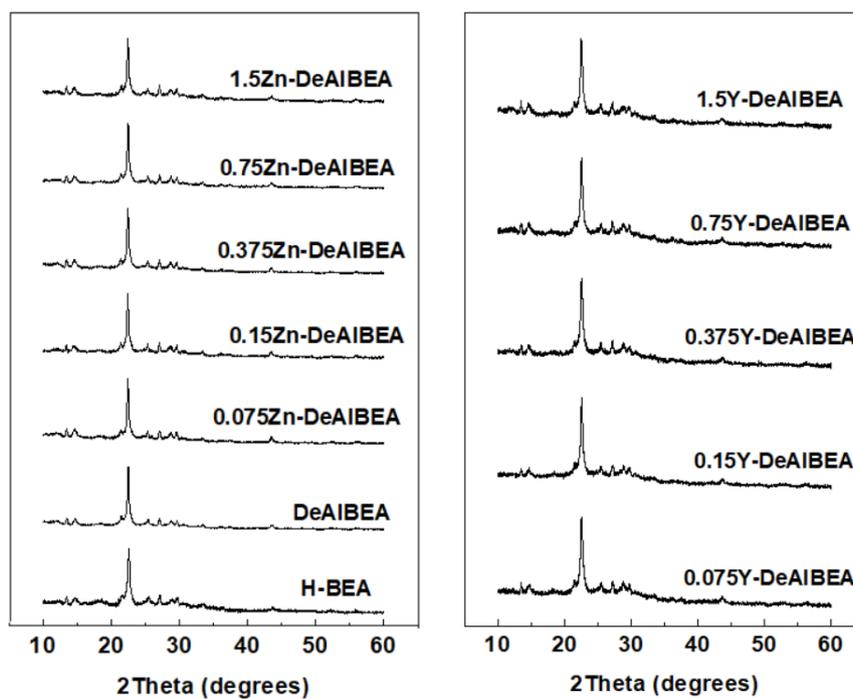


Figure S1. XRD patterns for H-BEA, DeAlBEA, Zn-DeAlBEA and Y-DeAlBEA.

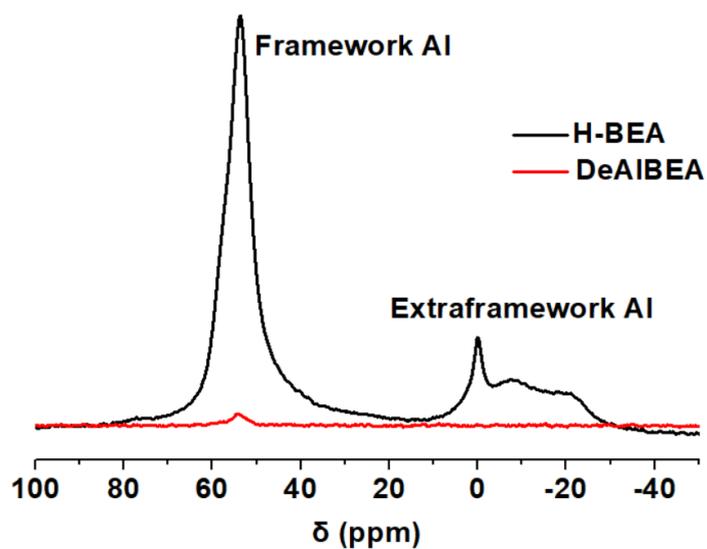


Figure S2.  $^{27}\text{Al}$  NMR result of HBEA and DeAlBEA samples.

**Table S2. ICP Result for Zn-DeAlBEA and Y-DeAlBEA Samples**

M/Al ratio	Introduced Zn wt%	Measured Zn wt%	Introduced Y wt%	Measured Y wt%
0.075	0.4	0.47	0.55	0.51
0.15	0.8	0.81	1.1	1.06
0.30	1.6	1.63	2.2	2.07
0.75	4	4.58	5.5	4.94
1.50	8	8.44	11	9.24

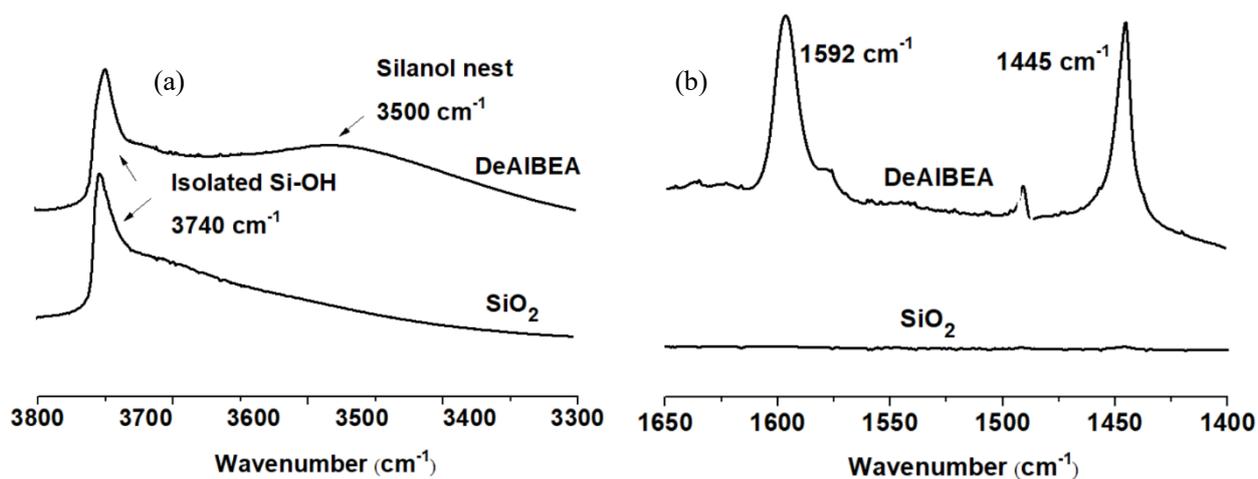


Figure S3. FTIR (a) and pyridine adsorbed FTIR (b) spectra of DeAlBEA and  $\text{SiO}_2$  samples.

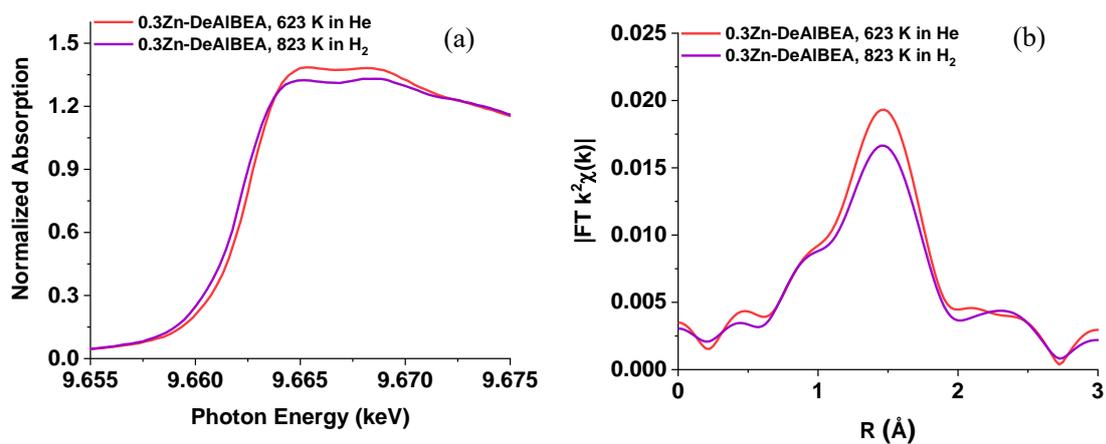


Figure S4. X-ray absorption spectroscopic analysis of 0.3Zn-DeAlBEA (red) before and after H<sub>2</sub> treatment at 823 K. XANES (a); Fourier transforms of EXAFS data (b).

**Table S3. EXAFS Fits for 0.3Zn-DeAlBEA after Treatment in Flowing H<sub>2</sub> at 823 K**

Treatment	XANES (keV)	Coordination number	Bond distance (Å)	$\Delta\sigma^2$ ( $\times 10^{-3}$ )	$E_0$ (eV)
623 K in He	9.6626	4.0	1.97	0.0083	2.5
823 K in H <sub>2</sub>	9.6622	3.4	1.97	0.0083	2.5

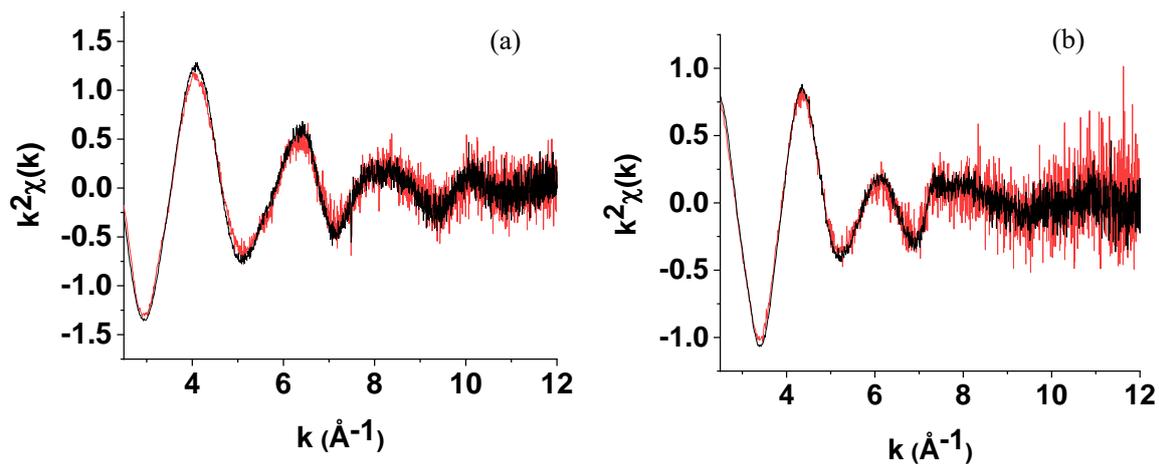


Figure S5. The Zn K-edge  $k^2$ -weighted EXAFS of 0.15Zn-DeAlBEA (red) and 0.3Zn-DeAlBEA (black) (a). The Y K-edge  $k^2$ -weighted EXAFS of 0.15Y-DeAlBEA (red) and 0.3Y-DeAlBEA (black) (b). The samples were treated at 623 K in flowing He and scanned at r.t.

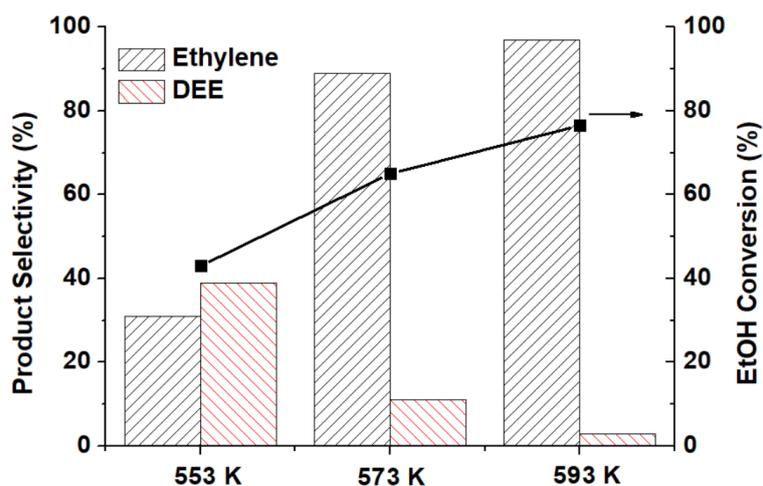


Figure S6. EtOH conversion over DeAlBEA catalyst. Catalyst mass = 50 mg, TOS = 30 min,  $P_{\text{EtOH}} = 5.3$  kPa, total flow rate at STP = 25 mL/min

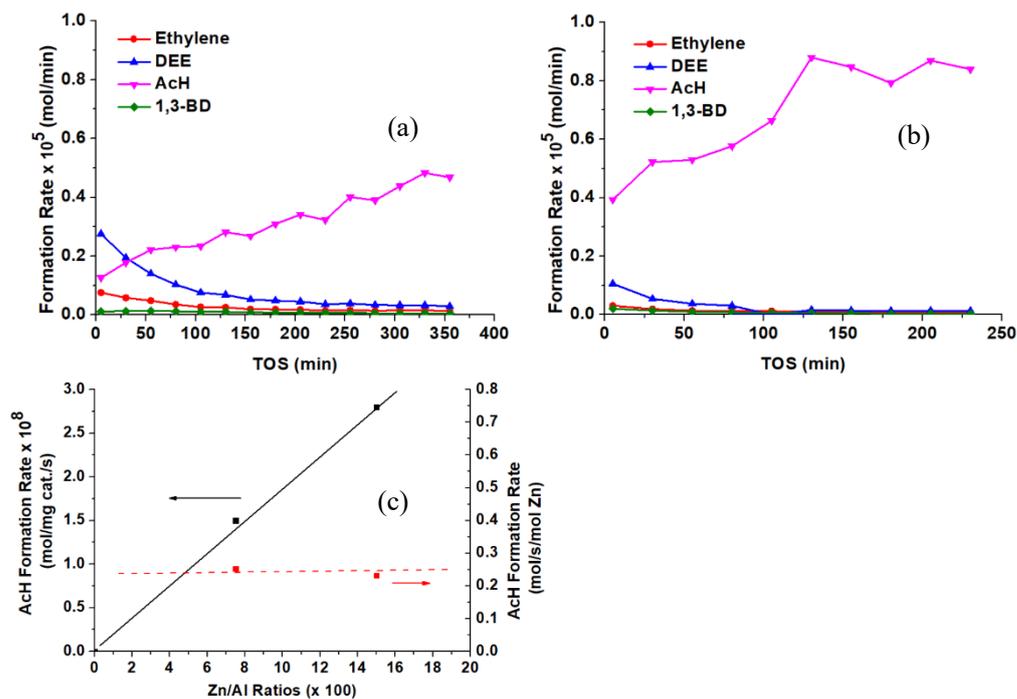


Figure S7. Evolution of AcH formation rate with TOS over 0.075Zn-DeAlBEA (a) and 0.15Zn-DeAlBEA (b) catalysts at 573 K; and the normalized AcH formation rate by catalyst mass and Zn molar amount (c). Catalyst mass = 5 mg, total flow rate at STP = 42.5 mL/min,  $P_{\text{EtOH}} = 5.3$  kPa

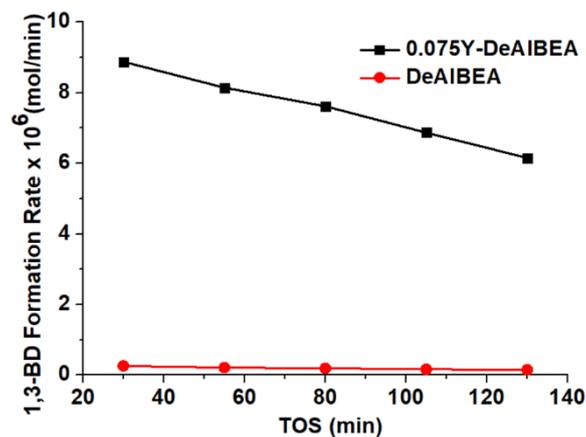


Figure S8. Comparison of 1,3-BD formation rate between 0.075Y-DeAlBEA and DeAlBEA catalysts. Catalyst mass = 50 mg,  $T = 593$  K,  $P_{\text{EtOH}} = 5.8$  kPa,  $P_{\text{AcH}} = 1.4$  kPa, total flow rate at STP = 24 mL/min.

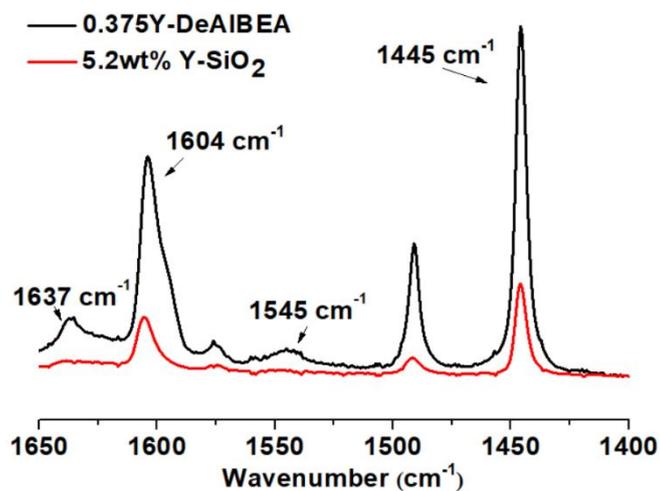


Figure S9. FTIR spectra of pyridine adsorbed on 0.375Y-DeAlBEA and 5.2 wt% Y-SiO<sub>2</sub> materials.

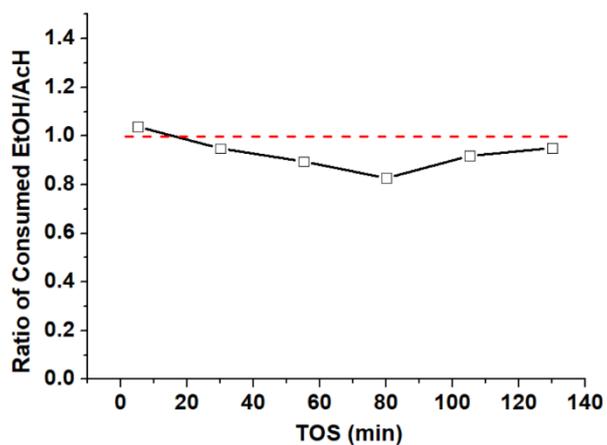


Figure S10. The observed ratio of consumed EtOH and AcH for 1,3-BD generation over 0.075Y-DeAlBEA. Catalyst mass = 50 mg, T = 593 K, total flow rate at STP = 24 mL/min, P<sub>EtOH</sub> = 5.8 kPa, P<sub>AcH</sub> = 1.4 kPa.

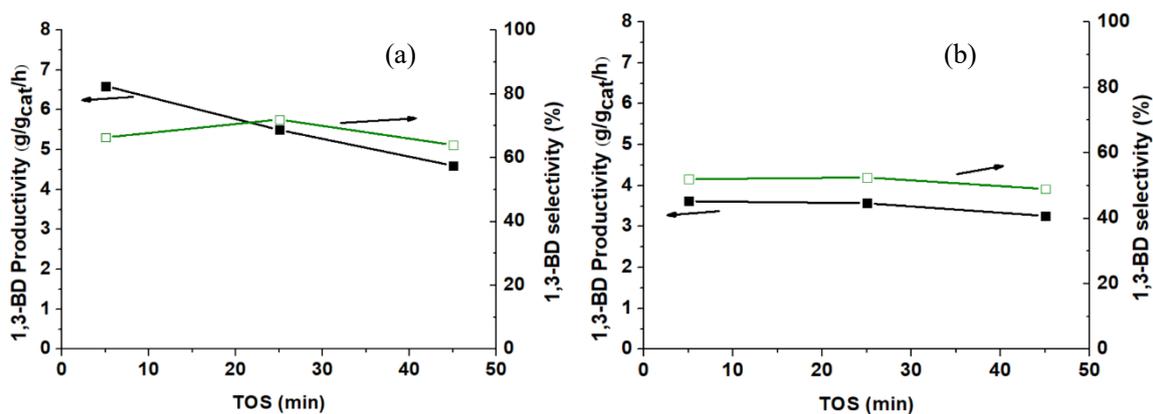


Figure S11. Evolution of 1,3-BD productivity and selectivity with TOS for 0.375Y-DeAlBEA (a) and 0.15Zn-0.225Y-DeAlBEA (b). T = 673 K, He flow rate = 40 mL/min, EtOH flow rate = 0.25 mL/h, AcH flow rate = 0.15 mL/h for 0.375Y-DeAlBEA; T = 673 K, He flow rate = 40 mL/min, EtOH flow rate = 0.32 mL/h for 0.15Zn-0.225Y-DeAlBEA.

### Derivation of EtOH dehydrogenation kinetic equations over Zn single site

The elementary steps for the EtOH dehydrogenation over Zn single site is listed below and the meaning of each symbols for E, H<sub>2</sub>, A, \*<sub>1</sub>, E\* and H<sub>2</sub>\*<sub>1</sub> means:

E: ethanol; H<sub>2</sub>: hydrogen; A: acetaldehyde

\*<sub>1</sub>: Zn site

E\*<sub>1</sub>: ethanol adsorbed on Zn; A\*<sub>1</sub>: acetaldehyde adsorbed on Zn



Each above symbol in [] means the corresponding partial pressure or concentration. The active sites balance is:

$$[*_{1}]_{\text{total}} = [E*_{1}] + [A*_{1}] + [*_{1}] \quad (\text{S1})$$

$$[E*_{1}] = K_E[E][*_{1}] \quad (\text{S2})$$

Assuming A desorption is very fast and [A\*<sub>1</sub>] can be ignored,

$$[*_{1}]_{\text{total}} = K_E[E][*_{1}] + [*_{1}] \quad (\text{S3})$$

$$[*_{1}] = [*_{1}]_{\text{total}} / (1 + K_E[E]) \quad (\text{S4})$$

Assuming rate limiting step for AcH formation is abstraction of a-H

$$r_A = k_I[E*_{1}] \quad (\text{S5})$$

Substitution of [E\*<sub>1</sub>] from Equation (S2) gives:

$$r_A = k_I K_E [E][*_{1}] \quad (\text{S6})$$

$$\text{TOF} = r_A / [*_{1}]_{\text{total}} \quad (\text{S7})$$

Substitution of [\*<sub>1</sub>]<sub>total</sub> from Equation (S4) gives:

$$\text{TOF} = \frac{k_I K_E [E]}{1 + K_E [E]} \quad (\text{S8})$$

Representing Equation (S8) in partial pressure notation yields Equation (S9), which is equivalent to Equation 1 in the Main Manuscript:

$$r_{AcH} = \frac{k_I K_E P_{EtOH}}{1 + K_E P_{EtOH}} \quad (\text{S9})$$

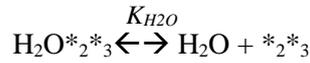
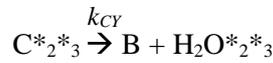
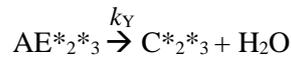
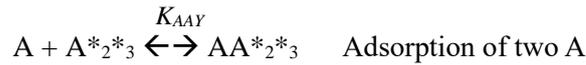
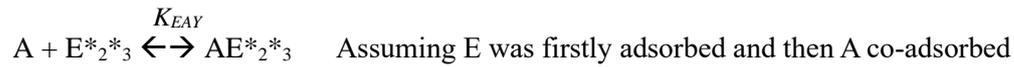
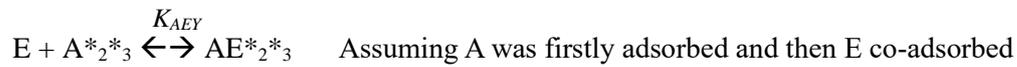
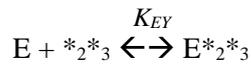
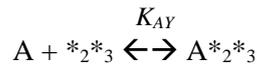
### Derivation of EtOH and AcH to 1,3-BD kinetic equations

The meaning of each symbol is listed below for E, A, B, C, \*<sub>1</sub>, \*<sub>2</sub>, \*<sub>3</sub>, \*<sub>2</sub>\*<sub>3</sub>:

E: ethanol; A: acetaldehyde; B: 1,3-BD; C: crytol alcohol

\*<sub>1</sub>: Zn site; \*<sub>2</sub>: Y site, \*<sub>3</sub>: Si-OH site, \*<sub>2</sub>\*<sub>3</sub>: Y with adjacent Si-OH site.

### For 1,3-BD generated over Y single site with adjacent Si-OH:



The active sites balance is:

$$[*_{2*3}]_{\text{total}} = [E*_{2*3}] + [A*_{2*3}] + [AE*_{2*3}] + [AA*_{2*3}] + [C*_{2*3}] + [H_2O*_{2*3}] + [*_{2*3}]$$

(S10)

$$[E*_{2*3}] = K_{EY}[E][*_{2*3}] \quad (S11)$$

$$[A*_{2*3}] = K_{AY}[A][*_{2*3}] \quad (S12)$$

$$[AE*_{2*3}] = K_{AEY}[E][A*_{2*3}] + K_{EAY}[A][E*_{2*3}] \quad (S13)$$

$$= K_{AEY}K_{AY}[E][A][*_{2*3}] + K_{EAY}K_{EY}[A][E][*_{2*3}]$$

$$[AA*_{2*3}] = K_{AA Y}K_{AY}[A]^2[*_{2*3}] \quad (S14)$$

Assuming conversion of crytol alcohol and H<sub>2</sub>O desorption is very fast

$$[*_2*_3]_{total} = [*_2*_3] + [A*_2*_3] + [E*_2*_3] + [AE*_2*_3] + [AA*_2*_3] \quad (S15)$$

Substitution of  $[A*_2*_3]$ ,  $[E*_2*_3]$ ,  $[AE*_2*_3]$  and  $[AA*_2*_3]$  from Equation (S11), (S12), (S13) and (S14) gives:

$$[*_2*_3] = \frac{[*_2*_3]_{total}}{1+K_{EY}[E]+K_{AY}[A]+K_{AAY}K_{AY}[A]^2+K_{AEY}K_{AY}[A][E]+K_{EAY}K_{EY}[A][E]} \quad (S16)$$

Assuming the C-C coupling step is the rate-determining step:

$$r_{C-C} = k_Y[AE*_2*_3] \quad (S17)$$

Substitution of  $[AE*_2*_3]$  from Equation (S13) gives:

$$r_{C-C} = k_Y(K_{AEY}K_{AY}[E][A][*_2*_3] + K_{EAY}K_{EY}[A][E][*_2*_3]) \quad (S18)$$

Combination of equation (S18) with (S16) gives:

$$TOF = r_{C-C}/[*_2*_3]_{total} = \frac{k_Y[A][E](K_{AEY}K_{AY}+K_{EAY}K_{EY})}{1+K_{EY}[E]+K_{AY}[A]+K_{AAY}K_{AY}[A]^2+[A][E](K_{AEY}K_{AY}+K_{EAY}K_{EY})} \quad (S19)$$

We define  $K_Y = K_{AEY}K_{AY} + K_{EAY}K_{EY}$

$$TOF = \frac{k_Y K_Y [A][E]}{1+K_{EY}[E]+K_{AY}[A]+K_{AAY}K_{AY}[A]^2+K_Y[A][E]} \quad (S20)$$

Representing Equation (S20) in partial pressure notation yields Equation (S21), which is equivalent to Equation 3 in the Main Manuscript:

$$r_{C-C} = \frac{k_Y K_Y P_{EtOH} P_{AcH}}{1+K_{EY} P_{EtOH} + K_{AY} P_{AcH} + K_{AAY} K_{AY} [P_{AcH}]^2 + K_Y P_{EtOH} P_{AcH}} \quad (S21)$$