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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

2020-08-01

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^{1,2}, Yanfei Zhang², Matthew A. Conrad³, Christopher K. Russell³,
Jeffrey Miller³, and Alexis T. Bell^{*1,2}

¹Chemical Sciences Division
Lawrence Berkeley National Laboratory
Berkeley, CA 94720

²Department of Chemical and Biomolecular Engineering
University of California
Berkeley, CA 94720

³Davidson School of Chemical Engineering
Purdue University
West Lafayette, IN 47907

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Table S1. Microporous Surface Area for Different Samples

Catalyst	Microporous surface area
	m ² 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}Al NMR result of HBEA and DeAlBEA samples.

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

M/Al ratio	Introduced Zn	Measured Zn	Introduced Y	Measured Y
	wt%	wt%	wt%	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 SiO_2 samples.

Figure S4. X-ray absorption spectroscopic analysis of 0.3Zn-DeAlBEA (red) before and after H₂ treatment at 823 K. XANES (a); Fourier transforms of EXAFS data (b).

Table S3. EXAFS Fits for 0.3Zn-DeAlBEA after Treatment in Flowing H₂ 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 ₂	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, $P_{\text{EtOH}} = 5.3 \text{ kPa}$, 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-SiO₂ materials.

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

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, H₂, A, *, *₁, E* and H₂*₁ means:

E: ethanol; H₂: hydrogen; A: acetaldehyde

*₁: Zn site

E*₁: ethanol adsorbed on Zn; A*₁: 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*₁] 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*₁] 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 [*₁]_{total} 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, $*_1$, $*_2$, $*_3$, $*_2*_3$:

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

$*_1$: Zn site; $*_2$: Y site, $*_3$: Si-OH site, $*_2*_3$: 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_2O 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:

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