

Supporting Information

Mechanism and Kinetics of Isobutene Formation from Ethanol and Acetone over $\text{Zn}_x\text{Zr}_y\text{O}_z$

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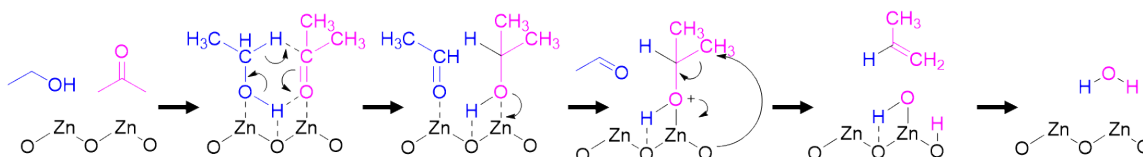
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Scheme S1: Production of propene from ethanol and acetone via MPV reduction of acetone to produce isopropanol, followed by dehydration to produce propene.

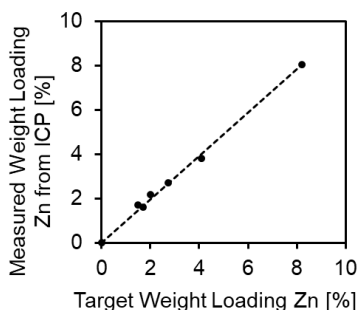


Figure S1: Target weight loading of Zn for incipient wetness impregnation method versus measured weight loading from ICP conducted by Galbriath Laboratories.

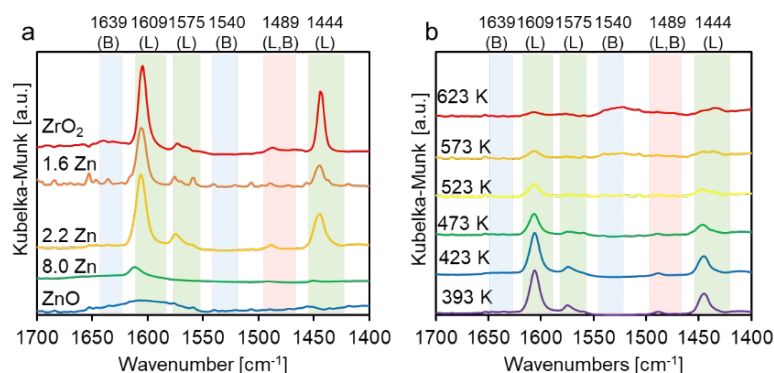


Figure S2: a) DRIFTS-py at 393 K for ZnO, ZrO₂, and Zn_xZr_yO_z with varying weight loadings of Zn. Catalysts diluted with KBr (250 mg KBr, 50 mg catalyst) except for ZnO which was not diluted by KBr, b) DRIFTS- py as a function of temperature over Zn_xZr_yO_z (2.2 wt% Zn).

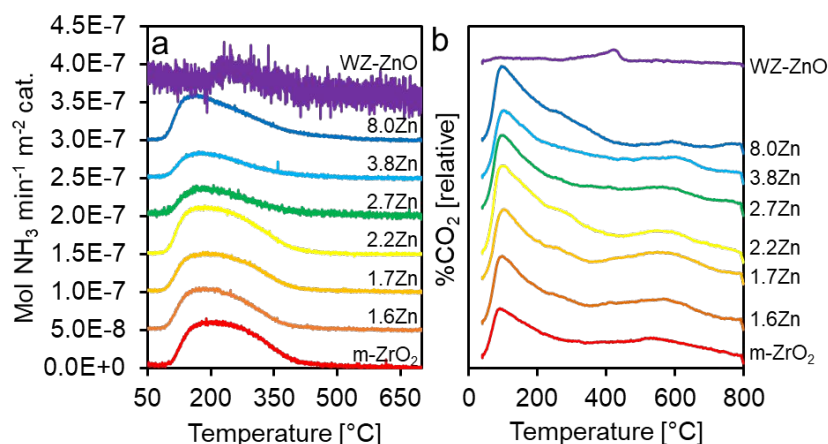


Figure S3: a) NH₃-TPD profiles of catalysts, b) CO₂-TPD profiles of catalysts.

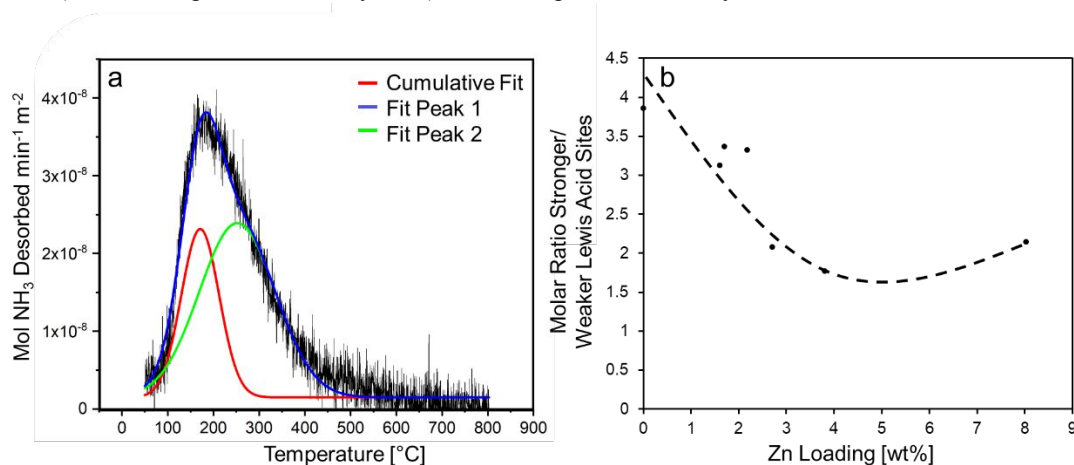


Figure S4: a) Representative Peak Deconvolution for NH₃ desorption as a function of temperature for Zn_xZr_yO_z (2.7wt% Zn), performed in Origin, b) Ratio of moles NH₃ desorbed from stronger Lewis acid sites (peak temperature 230 °C, Fit Peak 2) over weaker Lewis acid sites (peak temperature 160 °C, Fit Peak 1). Dashed lines are to guide the eye.

Table S1. Ratio of Stronger to Weaker Lewis Acid Sites on ZrO_2 and $\text{Zn}_x\text{Zr}_y\text{O}_z$ measured by NH_3 TPD.

Wt% Zn ($\text{Zn}_x\text{Zr}_y\text{O}_z$)	Molar Ratio of Stronger/ Weaker Lewis Acid Sites	Total Lewis Acidity ($\mu\text{mol NH}_3/\text{m}^2$)	Weak Lewis Acidity ($\mu\text{mol NH}_3/\text{m}^2$) ^a	Strong Lewis Acidity ($\mu\text{mol NH}_3/\text{m}^2$) ^b
0 (ZrO_2)	3.9	2.6	0.5	2.1
1.6	3.1	2.2	0.5	1.7
1.7	3.4	2.2	0.5	1.7
2.18	3.3	2.6	0.6	2.0
2.7	2.1	1.5	0.5	1.0
3.8	1.8	1.8	0.6	1.2
8.02	2.1	2.6	0.8	1.8

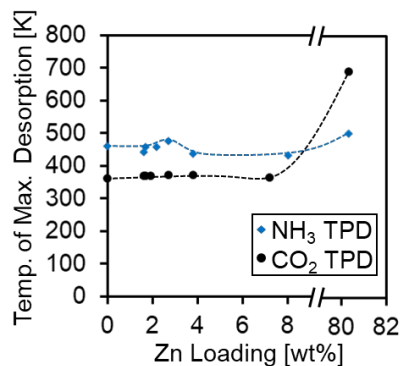


Figure S5: Temperature of maximum desorption of NH_3 (blue diamond) and CO_2 (black circle) during temperature-programmed-desorption (TPD) experiments for ZrO_2 , ZnO , and the $\text{Zn}_x\text{Zr}_y\text{O}_z$ catalysts.

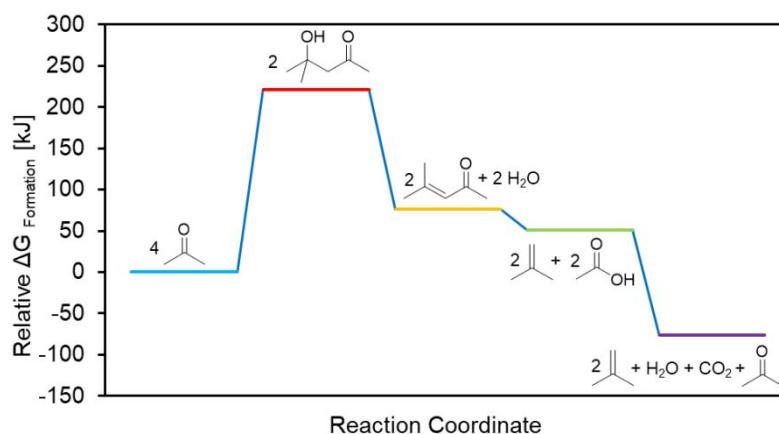


Figure S6: Gas phase free energies of formation calculated from DFT. Values are normalized relative to acetone and are expressed on a basis of kJ per number of moles shown by the stoichiometry for each intermediate step. Details for Qchem Calculations: Geometry minimization: exchange omega B97X-D, basis 6-31G**, Frequency calculation: exchange omega B97X-D, basis 6-31G**, Single point energy: exchange omega B97X-D, basis 6-311++G(3df,3pd).

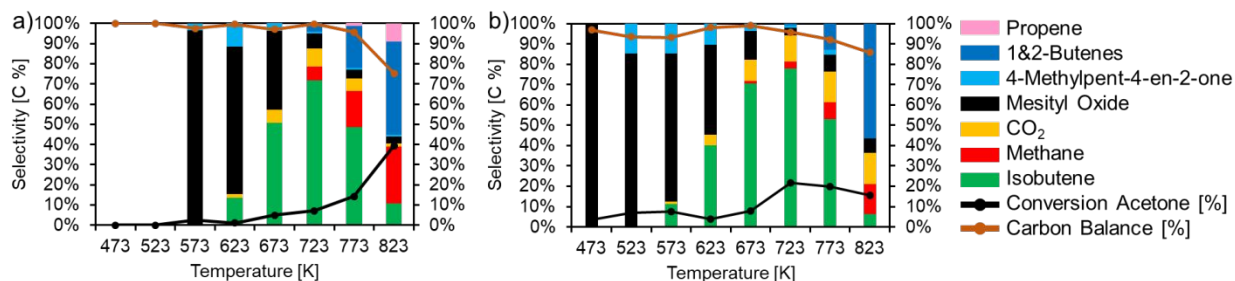


Figure S7: Effect of temperature on the acetone to isobutene reaction. Reaction Conditions: 0.4 kPa acetone, 17.8 kPa H₂O, S/C 8, 50 mL min⁻¹ He, a) 283.5 mg ZnO, b) 20.5 mg Zn_xZr_yO_z (2.2 wt% Zn). Catalyst deactivation for both catalysts began at 773 K, data recorded is from initial rate.

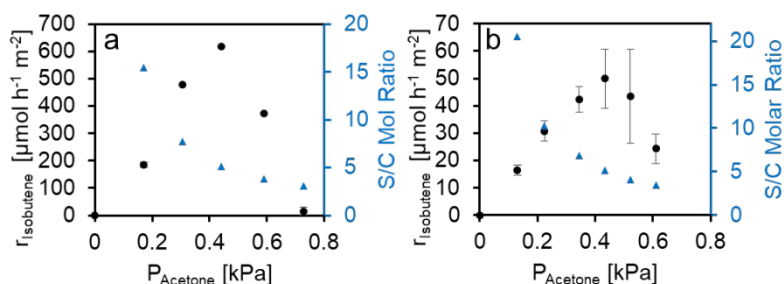


Figure S8: Effect of steam to carbon ratio on reaction rates for the acetone to isobutene reaction over a) Zn_xZr_yO_z (2.2 wt% Zn) and b) ZnO (61.4 mg). Reaction conditions: 723 K, 150 mL min⁻¹ He with a) 15 kPa H₂O and b) 13 kPa H₂O.

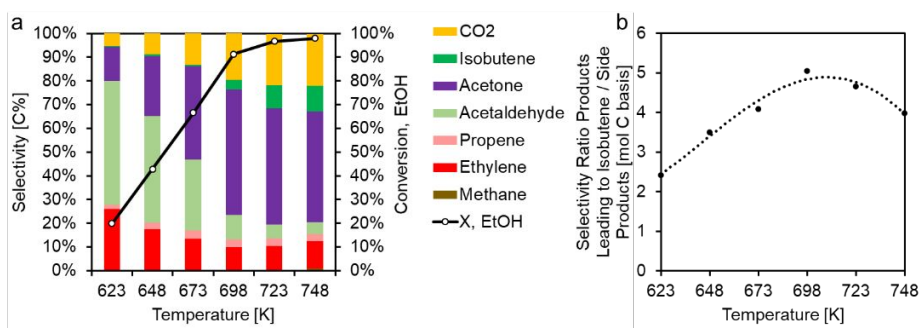


Figure S9: a) Effect of temperature on the ethanol to isobutene reaction over Zn_xZr_yO_z (2.2 wt% Zn). Reaction Conditions: 0.1 kPa acetone, 30 kPa H₂O, 50 mL min⁻¹ He, atmospheric pressure, b) Selectivity ratio of productive products leading to isobutene (acetaldehyde, acetone, and isobutene) over undesired side products (methane, ethylene, and propene), demonstrating that 698 K is the ideal temperature for maximizing the productive cascade reaction.

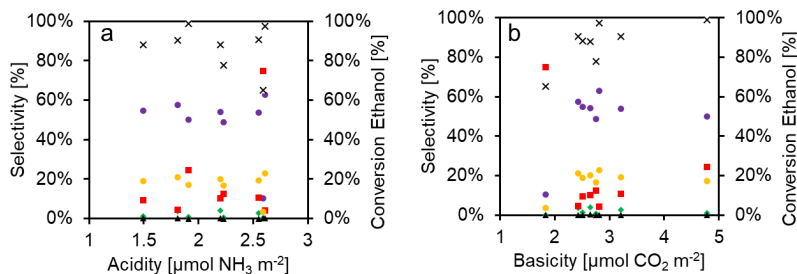


Figure S10: a) Effect of acidity (measured by NH₃-TPD) on the selectivity for the ethanol to isobutene reaction, b) effect of basicity (measured by CO₂-TPD) on the ethanol to isobutene reaction. Reaction conditions: 698 K, 1 kPa EtOH, S/C 4, 50 mL min⁻¹ He, WHSV 0.7, spacetime normalized by BET surface area.

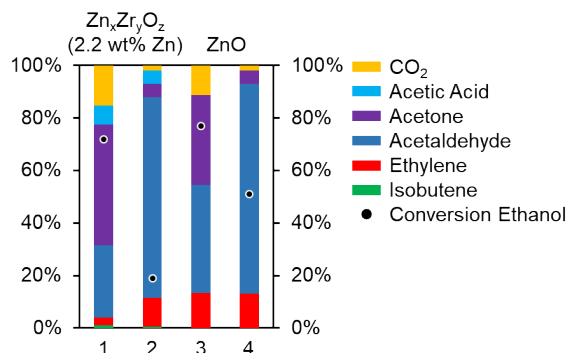


Figure S11: Ethanol reactions over $\text{Zn}_x\text{Zr}_y\text{O}_z$ (2.2 wt% Zn) and ZnO in the presence and absence of water. Entries 1, 2: $\text{Zn}_x\text{Zr}_y\text{O}_z$ (2.2 wt% Zn) 4.8 mg, entries 3, 4: 58 mg ZnO, 0.2 kPa acetone, entries 1, 3: 13 kPa H_2O , entries 2, 4: 0 kPa H_2O , 150 mL min^{-1} He, 723 K. As observed by entries 1 and 2, in the absence water, the selectivity towards ethylene (red) increases over $\text{Zn}_x\text{Zr}_y\text{O}_z$ (2.2 wt% Zn) and the conversion dramatically decreases. Over ZnO (entries 3 and 4), the absence of water also decreases the conversion and significantly decreases the conversion of acetaldehyde to acetone.

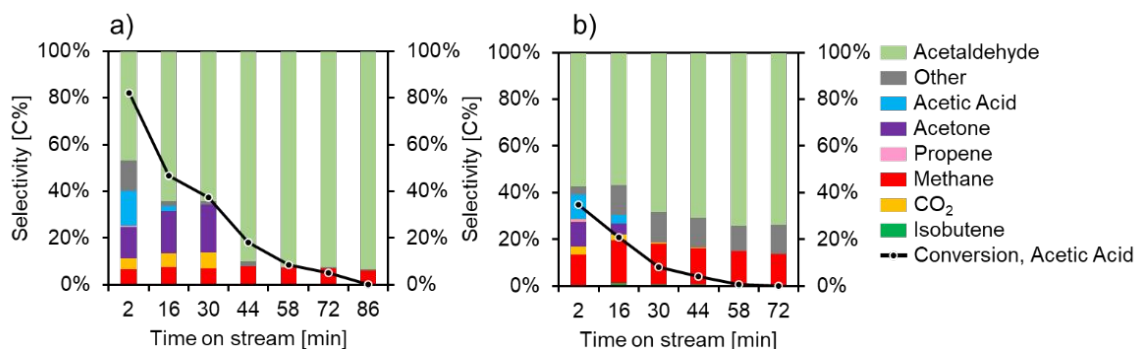


Figure S12: Reactions of ethanol and acetaldehyde mixtures in the absence of water over a) ZnO (60.1 mg), and b) $\text{Zn}_x\text{Zr}_y\text{O}_z$ 2.2 wt% Zn (4.8 mg). Reaction conditions: 0.11 kPa EtOH, 0.03 kPa acetaldehyde, 723 K, 150 mL min^{-1} He, atmospheric pressure.

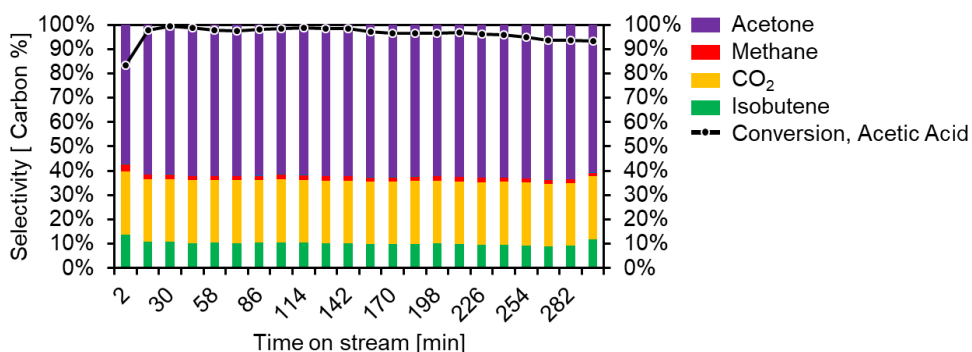


Figure S13: Effect of time on stream for the reaction of acetic acid to isobutene at 723 K. Reaction conditions: 22.3 mg $\text{Zn}_x\text{Zr}_y\text{O}_z$ 2.2 wt% Zn, 150 mL min^{-1} He, 0.21 kPa acetic acid, 11.4 kPa H_2O , S/C 5.4. Reaction was stable for over 5 h.

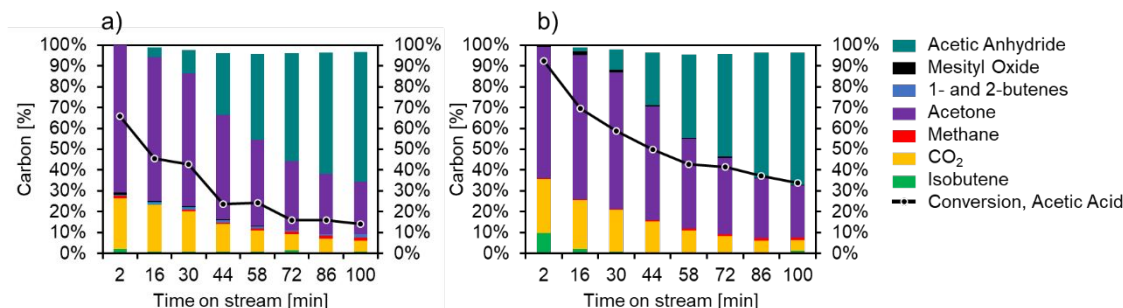


Figure S14: Reactions of acetic acid in the absence of water over a) ZnO and b) $\text{Zn}_x\text{Zr}_y\text{O}_z$ 2.2 wt% Zn. Reaction conditions: a) 723 K, 0.22 kPa acetic acid, 60.1 mg catalyst, 150 mL min^{-1} He; b) 723 K, 0.26 kPa acetic acid, 4.9 mg catalyst, 150 mL min^{-1} He.

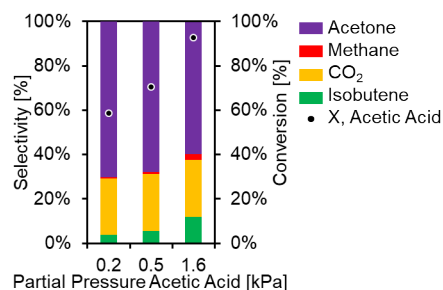


Figure S15: Effect of partial pressure for the reaction of acetic acid to produce isobutene over $\text{Zn}_x\text{Zr}_y\text{O}_z$ 2.2 wt% Zn. Reaction conditions: 723 K, 20.8 mg $\text{Zn}_x\text{Zr}_y\text{O}_z$ 2.2 wt% Zn, $15\text{-}150 \text{ mL min}^{-1}$ He, S/C 5.

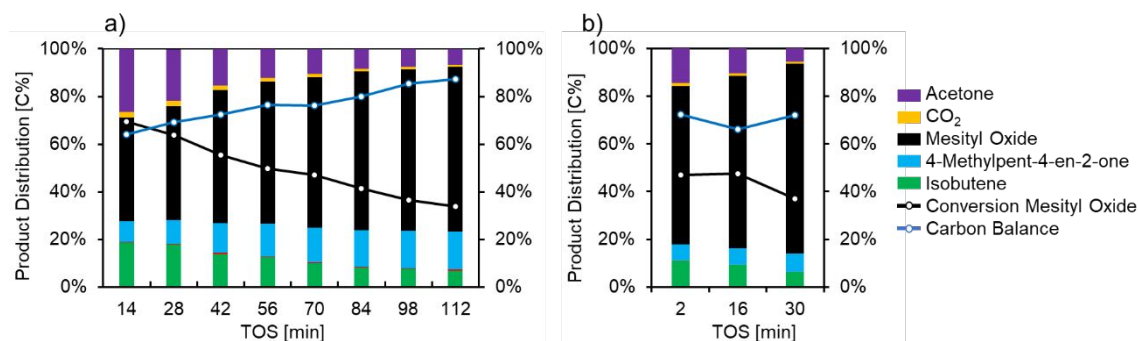


Figure S16: Deactivation of catalysts for the reaction of mesityl oxide and water over a) 4.8 mg $\text{Zn}_x\text{Zr}_y\text{O}_z$ 2.2 wt% Zn and b) 60.8 mg ZnO. Reaction Conditions: 723 K, 150 mL min^{-1} He, S/C 6.3, 13 kPa H_2O , 0.012 kPa initial 4-methylpent-4-en-2-one, 0.12 kPa initial Mesityl Oxide.

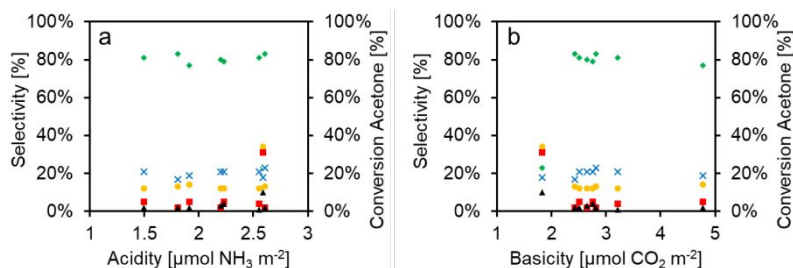


Figure S17: Conversion and selectivity for the acetone to isobutene reaction as a function of a) acidity [$\mu\text{mol NH}_3 \text{ m}^{-2}$] and b) basicity [$\mu\text{mol CO}_2 \text{ m}^{-2}$]. Reaction conditions: 698 K, 0.5 kPa acetone, 30 kPa H_2O , S/C 8.2, 50 mL min^{-1} He, 1 m^2 catalyst.

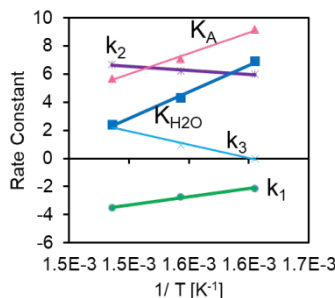


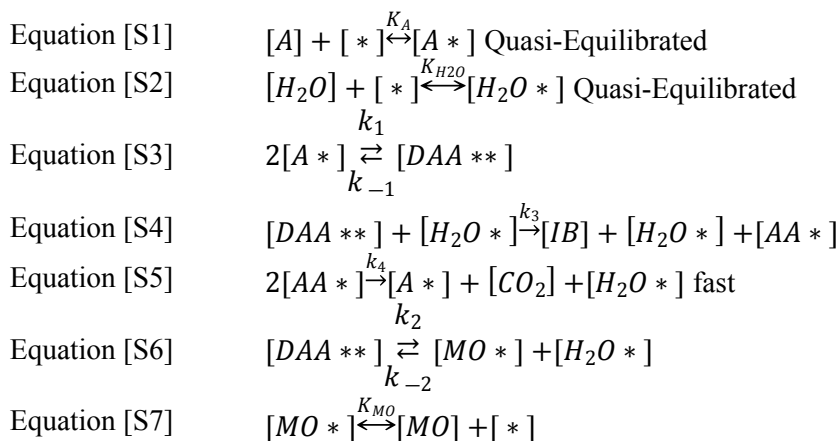
Figure S18: Arrhenius plots for rate constants given in **Table S2**.

Table S2. Kinetic Parameters from Model 2.

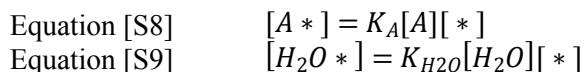
T [K]	k_1 [$\mu\text{mol h}^{-1} \text{m}^{-2}$]	k_2 [$\mu\text{mol h}^{-1} \text{m}^{-2}$]	k_3 [$\mu\text{mol h}^{-1} \text{m}^{-2} \text{kPa}^{-1}$]	K_A [kPa^{-1}]	k_{H_2O} [kPa^{-1}]	k_{-1} [$\mu\text{mol h}^{-1} \text{m}^{-2}$]
623	0.12	400	1	9000	1000	1000
648	0.065	500	2.6	1200	75	1000
673	0.03	800	10	300	11	1000
Apparent E_A [kJ mol ⁻¹]	-96 ± 8	48 ± 11	160 ± 19			
Apparent ln[A]	-21 ± 2	15 ± 2	31 ± 4			
ΔH_{ads} [kJ mol ⁻¹]				-238 ± 20	-315 ± 20	
ΔS [kJ mol ⁻¹ K ⁻¹]				0.3 ± 0.03	0.45 ± 0.03	

Derivation of Rate expressions for isobutene formation:

The elementary steps for the formation of isobutene from acetone are given by equations [S1]-[S7], where the partial pressures of the reactants and intermediates are given by: acetone [A], water [H₂O], diacetone alcohol [DAA**], acetic acid [AA*], carbon dioxide [CO₂], isobutene [IB], and mesityl oxide [MO]. The active site, [*] represents a Lewis acid/base pair.



Assuming steps in equations [S1] and [S2] are quasi-equilibrated:



Applying pseudo steady state (PSSH) approximation to [DAA**]:

Equation [S10]
$$\frac{d[DAA^{**}]}{dt} = k_1[A^*]^2 - k_{-1}[DAA^{**}] - k_2[DAA^{**}] + k_{-2}[MO^*][H_2O^*] - k_3[DAA^{**}]$$

Rearrangement of Equation [S10] yields Equation [S11]:

Equation [S11]
$$[DAA^{**}] = \frac{k_1[A^*]^2 + k_{-2}[MO^*][H_2O^*]}{(k_{-1} + k_2 + k_3[H_2O])}$$

Substitution of $[A^*]$ and $[H_2O^*]$ from Equations [S8] and [S9], and assuming surface mesityl oxide concentration is low yields Equation [S12]:

Equation [S12]
$$[DAA^{**}] = \frac{k_1 K_A^2 [A]^2 [^*]^2}{(k_{-1} + k_2 + k_3[H_2O])}$$

Model 1: Assuming rate limiting step for isobutene formation is C-C coupling of acetone:

Equation [S13]
$$r_{IB} = k_1[A^*]^2 - k_{-1}[DAA^{**}]$$

Substitution of $[DAA^{**}]$ from Equation [S12] into Equation [S13] yields Equation [S14]:

Equation [S14]
$$r_{IB} = k_1[A^*]^2 - k_{-1} \left(\frac{k_1 K_A^2 [A]^2 [^*]^2}{(k_{-1} + k_2 + k_3[H_2O])} \right)$$

Substitution of $[A^*]$ from Equation [S8] and rearrangement gives:

Equation [S15]
$$\frac{r_{IB}}{[^*]^2} = k_1 K_A^2 [A]^2 - k_{-1} \left(\frac{k_1 K_A^2 [A]^2}{(k_{-1} + k_2 + k_3[H_2O])} \right)$$

The Site Balance is given by Equation [S16], where it is assumed that surface mesityl oxide concentration is low, and all sites are occupied by either acetone or water:

Equation [S16]
$$L_1 = [A^*] + [H_2O^*]$$

Substitution of $[A^*]$ and $[H_2O^*]$ from Equations [S8] and [S9] yields Equation [S17]:

Equation [S17]
$$\frac{L_1}{[^*]} = (K_A[A] + K_{H_2O}[H_2O])$$

Substitution of the Site Balance in Equation [S17] for $[^*]$ into Equation [S15] yields Equation [S18]:

Equation [S18]
$$r_{IB} = \frac{k_1 K_A^2 [A]^2 - k_{-1} \left(\frac{k_1 K_A^2 [A]^2}{(k_{-1} + k_2 + k_3[H_2O])} \right)}{(K_A[A] + K_{H_2O}[H_2O])^2}$$

Representing Equation [S18] in partial pressure notation yields Equation [S19], which is equivalent to Equation 1 in the Main Manuscript:

$$\text{Equation [S19]} \quad r_{IB} = \frac{k_1 K_A^2 P_A^2 - k_{-1} \left(\frac{k_1 K_A^2 P_A^2}{(k_{-1} + k_2 + k_3 P_{H_2O})} \right)}{(K_A P_A + K_{H_2O} P_{H_2O})^2}$$

Model 2: Assuming rate limiting step is the decomposition of diacetone alcohol:

$$\text{Equation [S20]} \quad r_{IB} = k_3 [DAA^{**}] [H_2O^*]$$

Substitution of [DAA**] and [H₂O*] from Equations [S12] and [S9] and rearrangement gives Equation [S21]:

$$\text{Equation [S21]} \quad \frac{r_{IB}}{[*]^3} = k_3 K_{H_2O} [H_2O] \frac{k_1 K_A^2 [A]^2}{(k_{-1} + k_2 + k_3 [H_2O])}$$

Substitute of the Site Balance given by Equation [S17] yields Equation [S22]:

$$\text{Equation [S22]} \quad r_{IB} = \frac{\frac{k_1 K_A^2 [A]^2 k_3 K_{H_2O} [H_2O]}{(k_{-1} + k_2 + k_3 [H_2O])}}{(K_A [A] + K_{H_2O} [H_2O])^3}$$

Representing Equation [S22] in partial pressure notation yields Equation [S23], which is equivalent to Equation 2 in the Main Manuscript:

$$\text{Equation [S23]} \quad r_{IB} = \frac{\frac{k_1 K_A^2 P_A^2 k_3 K_{H_2O} P_{H_2O}}{(k_{-1} + k_2 + k_3 P_{H_2O})}}{(K_A P_A + K_{H_2O} P_{H_2O})^3}$$