Supporting Information

Mechanistic insights into formation of butene isomers from 1-butanol in H-ZSM-5: DFT based microkinetic modelling

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S1. Statistical thermodynamic calculation

The molecular partition function q for gas-phase species is calculated from statistical thermodynamics [1] as follows:

$$q(V,T) = q_{trans}(V,T)q_{vib}(T)q_{rot}(T) \qquad \text{(S.1)}$$

q_{vib}, q_{trans} and q_{rot} correspond to vibrational, translational and rotational molecular partition function, respectively.

Translational partition function

$$q_{trans}(V,T) = \left[\frac{2\pi m k_B T}{h^2}\right]^{\frac{3}{2}} V \qquad \text{(S.2)}$$

Rotational partition function for non-linear molecule

$$q_{rot}(T) = \frac{\sqrt{\pi I_A I_B I_C}}{\sigma}\left(\frac{8\pi^2 k_B T}{h^2}\right)^{\frac{3}{2}} \qquad \text{(S.3)}$$

Vibrational partition function considering the zero-point vibrational energy (ZPVE) to be the zero reference point

$$q_{vib}(T) = \prod_{i}^{3n-6} \frac{1}{1-\exp\left(\dfrac{-h\nu_i}{k_B T}\right)} \qquad \text{(S.4)}$$

where, n is the number of atoms in the molecule, h is the Planck constant, k_B is the Boltzmann factor, T is the temperature, v_i represent the vibrational frequencies obtained by a full hessian calculation with VASP, m is the molecular mass. For gas phase molecules, the volume V is calculated using an ideal gas equation. I_A, I_B, and I_C are the principal moments of inertia, σ is symmetry number.

On the other hand, the molecular partition function for immobile surface species ($q_{immobile}$) is calculated from statistical thermodynamics as follows:

$$q(T) = q_{immobile}(T) = q_{vib}(T) \qquad (S.5)$$

$$q_{vib}(T) = \prod_{i}^{3n} \frac{1}{1 - \exp\left(\dfrac{-hv_i}{k_B T}\right)} \qquad (S.6)$$

where, n is the number of atoms considered in the partial hessian calculation , h is the Planck constant, k_B is the Boltzmann factor, T is the temperature and v_i represent the vibrational frequencies obtained by a partial hessian calculation with VASP.

The total ensemble partition function Q(N,V,T) is given as:

$$Q(N,V,T) = \frac{[q(V,T)]^N}{N!} \qquad (S.7)$$

where, N is the number of particles and q is the molecular partition function .

Statistical thermodynamic calculation for internal energy (U), enthalpy (H), entropy (S) and Gibbs free energy (G) [Cramer]

$$U = E_{DFT-D2} + E_{ZPVE} + k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} \qquad (S.8)$$

$$H = U + PV = U + RT \qquad (S.9)$$

$$S = k_B \ln Q + k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} \qquad (S.10)$$

$$G = H - TS \qquad (S.11)$$

where, E_{DFT-D2} is energy from the DFT-D2 calculation, Q is total partition function, E_{ZPVE} is the zero point vibrational energy calculated as the sum of all the molecular vibrational energies at 0K ($E_{ZPVE} = \sum_i^{modes} \frac{1}{2} h \nu_i$).
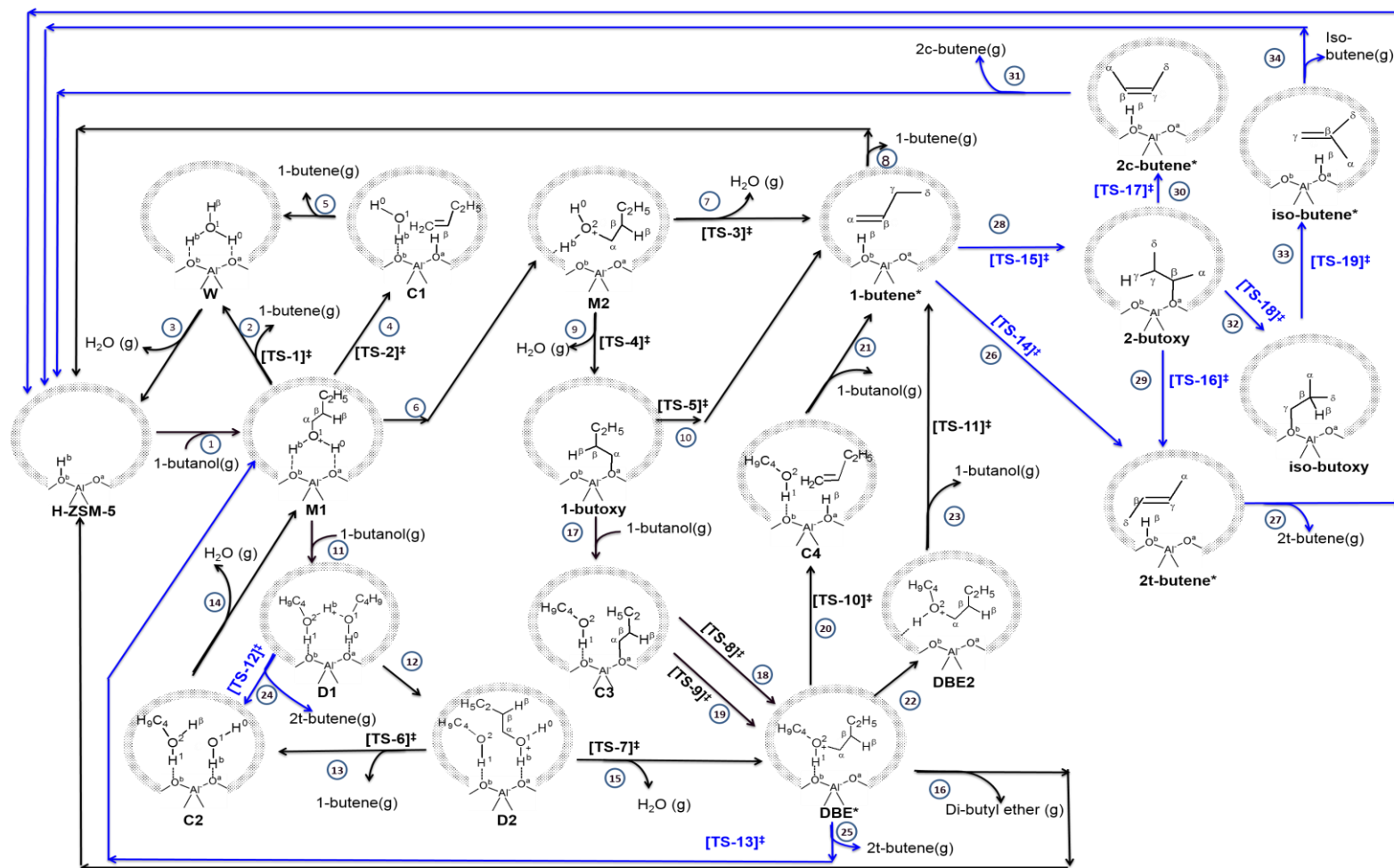
S2. Detailed reaction network

Figure S1: Detailed reaction network for 1-butanol dehydration to butene isomers in H-ZSM-5. Reaction steps in black and blue correspond to dehydration of 1-butanol to DBE / 1-butene[2] and 2t-butene/2c-butene/isobutene, respectively.

S3. Expression for the TOFs of individual reaction mechanisms

For reaction mechanism involving a unique activated step, the TOF for that mechanism is equal to the TOF of the corresponding unique activated step. For e.g.

$$TOF_{m1} = TOF_{R2} \quad\text{(S.12)}$$

$$TOF_{m2} = TOF_{R4} \quad\text{(S.13)}$$

$$TOF_{m3} = TOF_{R7} \quad\text{(S.14)}$$

$$TOF_{m4} = TOF_{R10} \quad\text{(S.15)}$$

$$TOF_{m5} = TOF_{R13} \quad\text{(S.16)}$$

$$TOF_{m6} = TOF_{R15} \quad\text{(S.17)}$$

$$TOF_{m7} = TOF_{R18} \quad\text{(S.18)}$$

$$TOF_{m8} = TOF_{R19} \quad\text{(S.19)}$$

$$TOF_{m9} = TOF_{R20} \quad\text{(S.20)}$$

$$TOF_{m10} = TOF_{R23} \quad\text{(S.21)}$$

$$TOF_{m11} = TOF_{R24} \quad\text{(S.22)}$$

$$TOF_{m12} = TOF_{R25} \quad\text{(S.23)}$$

$$TOF_{m13} = TOF_{R26} \quad\text{(S.24)}$$

For reaction mechanisms not having a unique activated step, a case specific algorithm is used for calculation of TOF. For e.g.

$TOF_{R29} > 0$, indicates $TOF_{m16} = TOF_{m18} = 0$

$TOF_{R29} < 0$, indicates $TOF_{m14}=0$

$TOF_{R30} > 0$ indicates $TOF_{m19} = 0$

$TOF_{R30} < 0$ indicates $TOF_{m15} = TOF_{m16}=0$

Under most of the reaction conditions used in the present study the conversion of 2-butoxide to 2t-butene* (R29) and 2c-butene* (R30) have a net positive value for their TOF.

If ($TOF_{R29} > 0$ and $TOF_{R30} > 0$)

$TOF_{m14} = TOF_{R29}$ ....(S.25)

$TOF_{m15} = TOF_{R30}$ ....(S.26)

$TOF_{m16} = 0$ ....(S.27)

$TOF_{m17} = TOF_{R28} - TOF_{m14} - TOF_{m15}$ ....(S.28)

$TOF_{m18} = 0$ ....(S.29)

$TOF_{m19} = 0$ ....(S.30)

When the gas phase and surface concentration of 2t-butene is very high, 2t-butene* can get converted into 2-butoxide (1.e $TOF_{R29} < 0$)

If ($TOF_{R29} < 0$ and $TOF_{R30} > 0$)

$TOF_{m14} = 0$ ....(S.31)

$TOF_{m19} = 0$ ....(S.32)

In order to obtain the TOF for reaction mechanisms m15-18, we have to solve for a linear set of algebraic equations

$$\text{TOF}_{m14} + \text{TOF}_{m15} + \text{TOF}_{m17} = \text{TOF}_{R28} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\text{(S.33)}$$

as $\text{TOF}_{m14} = 0$ equation 22 becomes

$$\text{TOF}_{m15} + \text{TOF}_{m17} = \text{TOF}_{R28} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\text{(S.34)}$$

$$\text{TOF}_{m16} + \text{TOF}_{m18} = -\text{TOF}_{R29} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\text{(S.35)}$$

$$\text{TOF}_{m15} + \text{TOF}_{m16} = \text{TOF}_{R30} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\text{(S.36)}$$

$$\text{TOF}_{m17} + \text{TOF}_{m18} + \text{TOF}_{m19} = \text{TOF}_{R32} = \text{TOF}_{R33} \dots\dots\dots\dots\text{(S.37)}$$

as $\text{TOF}_{m19} = 0$ equation 26 becomes

$$\text{TOF}_{m17} + \text{TOF}_{m18} = \text{TOF}_{R32} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\text{(S.38)}$$

The above set of equations (eqns. 23-25 and 27) can be directly solved to obtain TOF for mechanisms m15-18.

Alternatively, when TOF for the formation of isobutene is negligible ($\text{TOF}_{m17} \rightarrow 0$ and $\text{TOF}_{m18} \rightarrow 0$), equation reduces to a much simplified form.

$$\text{TOF}_{m15} = \text{TOF}_{R28} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\text{(S.39)}$$

$$\text{TOF}_{m16} = -\text{TOF}_{R29} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\text{(S.40)}$$

Lastly, a scenario involving a net positive TOF for conversion of 2c-butene* to 2-butoxy (i.e., $\text{TOF}_{R30} < 0$) is not observed under reaction conditions used in the present study.

References:

1. C. J. Cramer, *Essentials of computational chemistry : theories and models*, Wiley, Chichester Hoboken, NJ, 2nd edn., 2004.

2. M. John, K. Alexopoulos, M. F. Reyniers and G. B. Marin, *J Catal*, 2015, **330**, 28-45.