Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Dehydration of butanol towards butenes over MFI, FAU and MOR: influence of zeolite topology

Arno de Reviere[a,b], Dieter Gunst[a,b], Maarten Sabbe[a,b] Marie-Françoise Reyniers[b] and An Verberckmoes[a]

[a]Industrial Catalysis and Adsorption Technology (INCAT), Department of Materials, Textiles and Chemical Engineering, Ghent University, Valentin Vaerwyckweg 1, 9000 Ghent, Belgium

[b]Laboratory for Chemical Technology (LCT), Department of Materials, Textiles and Chemical Engineering, Ghent University, Technologiepark 125, 9052 Ghent, Belgium

Supporting information

(S1) Effect of chemical structure on activity

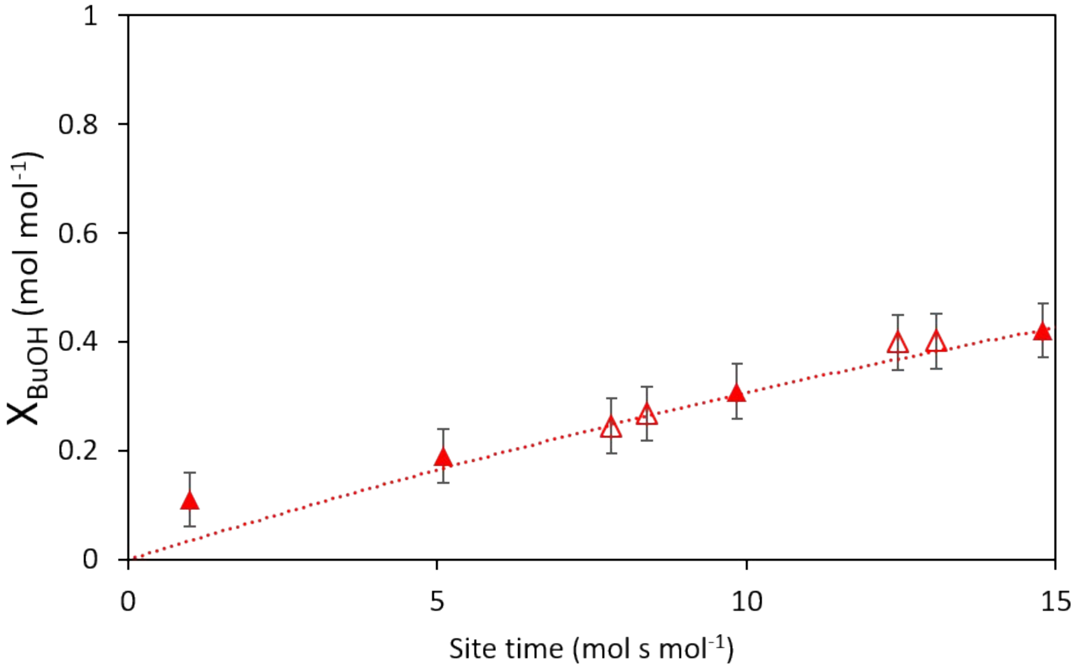

Figure S1. Comparison of butanol conversion as function of site time for H-MOR at 513 K, p^0_{BuOH} = 29 kPa, for the two butanol feeds: n-butanol (□, full symbol) and isobutanol (□, hollow symbol)

(S2) Effect of channel size on isobutene selectivity

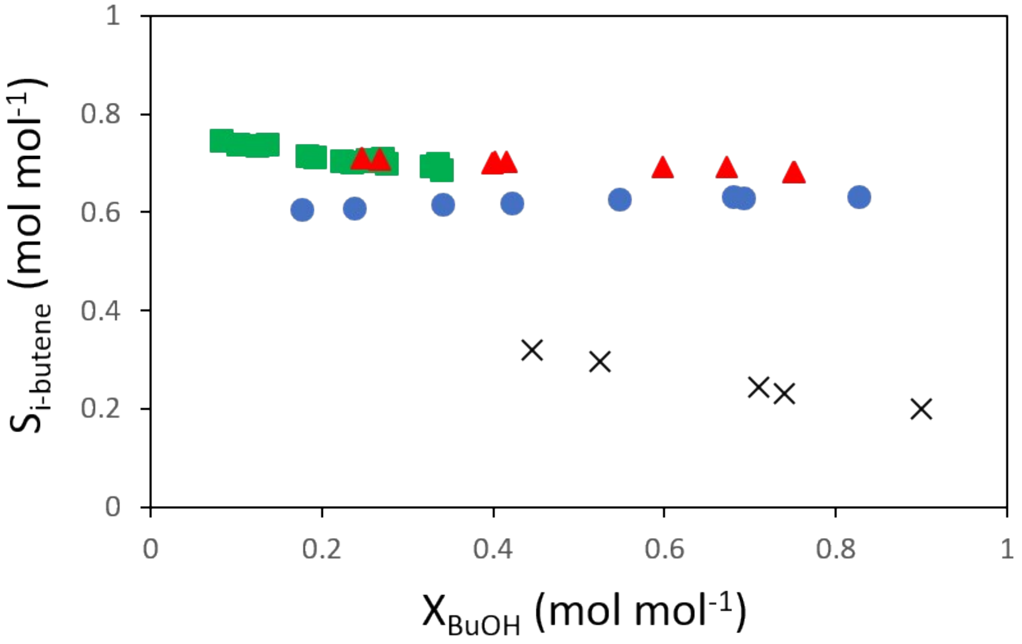

Figure S2. Selectivity of isobutene versus conversion of isobutanol for the three topologies investigated in this work at 513 K and comparison with isobutene selectivity by Buniazet et al.[1] *over H-FER at 523 K.* ● *= H-MFI,* ▰ *= H-FAU,* ▱ *= H-MOR and* × *= H-FER*

(S3) Elementary steps for the n-butanol dehydration over H-ZSM-5

Table S1: Elementary steps, reaction mechanisms (m1 – m18) and reaction pathways (A – J) for the 1-butanol dehydration reaction based on literature from John et al. [2-5] Per column it can be seen which elementary reaction steps contribute to the reaction mechanism (0 means not part of the mechanism).

Path		**A**					**B**			**C**		**D**	**E**	**F**		**G**	**H**	**I**	**J**
$^{n°}$ Elementary steps	Mechanism$_{n°}$	*m$_1$*	*m$_2$*	*m$_3$*	*m$_4$*	*m$_5$*	*m$_6$*	*m$_7$*	*m$_8$*	*m$_9$*	*m$_{10}$*	*m$_{11}$*	*m$_{12}$*	*m$_{13}$*	*m$_{14}$*	*m$_{15}$*	*m$_{16}$*	*m$_{17}$*	*m$_{18}$*
^{1} BuOH$_{(g)}$ + * ↔ M1		1	1	1	1	1	1	1	1	0	0	0	-1	0	0	0	-1	0	0
^{2} M1 ↔ W + 1-butene$_{(g)}$		1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
^{3} W ↔ H$_2$O + *		1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
^{4} M1 ↔ C1		0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
^{5} C1 ↔ W + 1-butene$_{(g)}$		0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
^{6} M1 ↔ M2		0	0	1	1	0	0	1	1	0	0	0	0	0	0	0	0	0	0
^{7} M2 ↔ 1-butene* + H$_2$O$_{(g)}$		0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
^{8} 1-butene* ↔ 1-butene$_{(g)}$ + *		0	0	1	1	0	0	0	0	1	1	0	0	-1	-1	0	0	-1	0
^{9} M2 ↔ butoxy + H$_2$O		0	0	0	1	0	0	1	1	0	0	0	0	0	0	0	0	0	0
^{10} butoxy ↔ 1-butene*		0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
^{11} M1 + BuOH$_{(g)}$ ↔ D1		0	0	0	0	1	1	0	0	0	0	1	0	0	0	1	0	0	0
^{12} D1 ↔ D2		0	0	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0
^{13} D2 ↔ C2 + 1-butene$_{(g)}$		0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
^{14} C2 ↔ M1 + H$_2$O$_{(g)}$		0	0	0	0	1	0	0	0	0	0	1	0	0	0	1	0	0	0
^{15} D2 ↔ DBE* + H$_2$O$_{(g)}$		0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
^{16} DBE* ↔ DBE$_{(g)}$ + *		0	0	0	0	0	1	1	1	-1	-1	0	-1	0	0	0	-1	0	0
^{17} butoxy + BuOH$_{(g)}$ ↔ C3		0	0	0	0	0	0	1	1	0	0	0	0	0	0	0	0	0	0
^{18} C3 ↔ DBE* (Sn2)		0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
^{19} C3 ↔ DBE* (Sn1)		0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0
^{20} DBE* ↔ C4		0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
^{21} C4 ↔ 1-butene* + BuOH$_{(g)}$		0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
^{22} DBE* ↔ DBE2		0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
^{23} DBE2 ↔ 1-butene* + BuOH$_{(g)}$		0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
^{24} D1 ↔ C2 + trans-2-butene$_{(g)}$		0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
^{25} DBE* ↔ M1 + trans-2-butene$_{(g)}$		0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0
^{26} 1-butene* ↔ trans-2-butene*		0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0
^{27} trans-2-butene* ↔ trans-2-butene$_{(g)}$ + *		0	0	0	0	0	0	0	0	0	0	0	0	1	1	0	0	0	-1
^{28} 1-butene* ↔ 2-butoxy		0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	1	0
^{29} 2-butoxy ↔ trans-2-butene*		0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	-1
^{30} 2-butoxy ↔ cis-2-butene*		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1
^{31} cis-2-butene* ↔ cis-2-butene$_{(g)}$ + *		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1

32 D1 ↔ C2 + cis-2-butene$_{(g)}$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0
33 DBE* ↔ M1 + cis-2-butene$_{(g)}$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0

Table S2: Elementary steps, reaction enthalpy, reaction entropy and their contribution to reaction free energy at 513 K for the 1-butanol dehydration over H-MFI, values obtained from Gunst et al. and John et al., reaction steps displayed in blue are dominant reaction steps throughout the conversion range at 513 K and an inlet partial pressure of 29 kPa.[2-6]

Reaction step	❐H_r (kJ mol^{-1})	❐S_r (kJ mol^{-1} K^{-1})	❐G_r (kJ mol^{-1})	|❐H_r |/|T❐S_r|^a
^{1} BuOH$_{(g)}$ + * ↔ M1	-125.00	-0.19200	-26.50	1.27
^{2} M1 ↔ W + 1-butene$_{(g)}$	107.00	0.20000	4.40	1.04
^{3} W ↔ $H_2O_{(g)}$ + *	53.16	0.12916	-13.10	0.80
^{4} M1 ↔ C1	74.00	0.07800	33.99	1.85
^{5} C1 ↔ W + 1-butene$_{(g)}$	33.00	0.12200	-29.59	0.53
^{6} M1 ↔ M2	82.11	-0.00484	84.59	33.07
^{7} M2 ↔ 1-butene* + $H_2O_{(g)}$	22.23	0.24600	-103.97	0.18
^{8} 1-butene* ↔ 1-butene$_{(g)}$ + *	55.82	0.08800	10.68	1.24
^{9} M2 ↔ butoxy + $H_2O_{(g)}$	22.00	0.16500	-62.65	0.26
^{10} butoxy ↔ 1-butene*	0.23	0.08100	-41.32	0.01
^{11} M1 + BuOH$_{(g)}$ ↔ D1	-125.70	-0.18300	-31.82	1.34
^{12} D1 ↔ D2	42.78	-0.00335	44.50	24.89
^{13} D2 ↔ C2 + 1-butene$_{(g)}$	69.00	0.16500	-15.65	0.82
^{14} C2 ↔ M1 + $H_2O_{(g)}$	49.08	0.15851	-32.24	0.60
^{15} D2 ↔ DBE* + $H_2O_{(g)}$	20.39	0.15700	-60.15	0.25
^{16} DBE* ↔ DBE$_{(g)}$ + *	166.15	0.19579	65.71	1.65
^{17} butoxy + BuOH$_{(g)}$ ↔ C3	-95.00	-0.17300	-6.25	1.07
^{18} C3 ↔ DBE* (Sn2)	-71.64	-0.01651	-63.17	8.46
^{19} C3 ↔ DBE* (Sn1)	-71.64	-0.01651	-63.17	8.46
^{20} DBE* ↔ C4	97.07	0.05110	70.86	3.70
^{21} C4 ↔ 1-butene* + BuOH$_{(g)}$	69.80	0.21941	-42.76	0.62
^{22} DBE* ↔ DBE2	58.00	0.00900	53.38	12.56
^{23} DBE2 ↔ 1-butene* + BuOH$_{(g)}$	108.87	0.26151	-25.28	0.81
^{24} D1 ↔ C2 + trans-2-butene$_{(g)}$	99.74	0.15001	22.78	1.30
^{25} DBE* ↔ M1 + trans-2-butene$_{(g)}$	85.65	0.15487	6.20	1.08
^{26} 1-butene* ↔ trans-2-butene*	-22.74	-0.00450	-20.43	9.85
^{27} trans-2-butene* ↔ trans-2-butene$_{(g)}$ + *	66.52	0.08086	25.04	1.60
^{28} 1-butene* ↔ 2-butoxy	-24.23	-0.07980	16.71	0.59
^{29} 2-butoxy ↔ trans-2-butene*	1.49	0.07530	-37.14	0.04
^{30} 2-butoxy ↔ cis-2-butene*	17.06	0.06690	-17.26	0.50
^{31} cis-2-butene* ↔ cis-2-butene$_{(g)}$ + *	54.36	0.09093	7.71	1.17
^{32} D1 ↔ C2 + cis-2-butene$_{(g)}$	103.15	0.15168	25.34	1.33
^{33} DBE* ↔ M1 + cis-2-butene$_{(g)}$	89.06	0.15654	8.75	1.11

[a] A value greater than 1 indicates that reaction enthalpy has a relatively larger contribution to the free energy than the reaction entropy

By comparing the enthalpic and entropic contributions to the free energy of the adsorption/desorption steps of n-butanol and DBE (1, 16 in Table S3), it is clear that for H-MFI the enthalpy is the strongest contributor under the studied reaction conditions, whereas for alkane adsorption, the entropy is already the strongest contributor to the free energy of adsorption at 513 K.[7] This difference between oxygenated molecules and the alkanes is due to the polar/apolar nature of the adsorbate. DBE and n-butanol are much more strongly adsorbed onto the surface due to their polarity, and the stronger loss in entropy is not able to counter this.

Table S3: Elementary steps, enthalpic (❐$H^{\ddagger}$) and entropic (❐$S^{\ddagger}$) barrier and their contribution to free energy barrier (❐$G^{\ddagger}$) at 513 K for the 1-butanol dehydration over H-MFI, values obtained from Gunst et al., reaction steps displayed in blue are dominant reaction steps, reactions for which no activation values are presented are assumed to be at equilibrium in the simulation as reported by John et al. [2-6]

Reaction step	❐$H^{\ddagger}$ (kJ mol^{-1})	❐$S^{\ddagger}$ (kJ mol^{-1} K^{-1})	❐$G^{\ddagger}$ (kJ mol^{-1})	|❐$H^{\ddagger}$|/|T❐$S^{\ddagger}$|^{a}
^{1} $BuOH_{(g)}$ + * ↔ M1				
^{2} M1 ↔ W + 1-butene$_{(g)}$	176	0.04	156.23	8.90
^{3} W ↔ $H_2O_{(g)}$ + *				
^{4} M1 ↔ C1	139	0.03	124.92	9.87
^{5} C1 ↔ W + 1-butene$_{(g)}$				
^{6} M1 ↔ M2				
^{7} M2 ↔ 1-butene* + $H_2O_{(g)}$	45.2	0.04	26.29	2.39
^{8} 1-butene* ↔ 1-butene$_{(g)}$ + *				
^{9} M2 ↔ butoxy + $H_2O_{(g)}$	49	0.03	34.24	3.32
^{10} butoxy ↔ 1-butene*	93	0.01	87.7	17.55
^{11} M1 + $BuOH_{(g)}$ ↔ D1				
^{12} D1 ↔ D2				
^{13} D2 ↔ C2 + 1-butene$_{(g)}$	118	0.03	104.07	8.47
^{14} C2 ↔ M1 + $H_2O_{(g)}$				
^{15} D2 ↔ DBE* + $H_2O_{(g)}$	99.42	0.02	88.44	9.06
^{16} DBE* ↔ $DBE_{(g)}$ + *				
^{17} butoxy + $BuOH_{(g)}$ ↔ C3				
^{18} C3 ↔ DBE* (Sn2)	61	-0.01	66.27	11.56
^{19} C3 ↔ DBE* (Sn1)	111	0.02	101.81	12.08
^{20} DBE* ↔ C4	159.01	0.03	145.56	11.82
^{21} C4 ↔ 1-butene* + $BuOH_{(g)}$				
^{22} DBE* ↔ DBE2				
^{23} DBE2 ↔ 1-butene* + $BuOH_{(g)}$	109	0.00	107.28	63.19
^{24} D1 ↔ C2 + trans-2-butene$_{(g)}$	163	0.05	136.86	6.24
^{25} DBE* ↔ M1 + trans-2-butene$_{(g)}$	171	0.05	145.94	6.82
^{26} 1-butene* ↔ trans-2-butene*	58.51	-0.06	91.56	1.77
^{27} trans-2-butene* ↔ trans-2-butene$_{(g)}$ + *				
^{28} 1-butene* ↔ 2-butoxy	47.57	-0.07	82.9	1.35
^{29} 2-butoxy ↔ trans-2-butene*	75.11	0.02	65.57	7.87
^{30} 2-butoxy ↔ cis-2-butene*	70.06	0.01	63.07	10.02
^{31} cis-2-butene* ↔ cis-2-butene$_{(g)}$ + *				
^{32} D1 ↔ C2 + cis-2-butene$_{(g)}$	165	0.05	138.86	6.31
^{33} DBE* ↔ M1 + cis-2-butene$_{(g)}$	176	0.05	150.94	70.02

(S4) Proposed reaction mechanism for the dehydration of isobutanol over zeolites

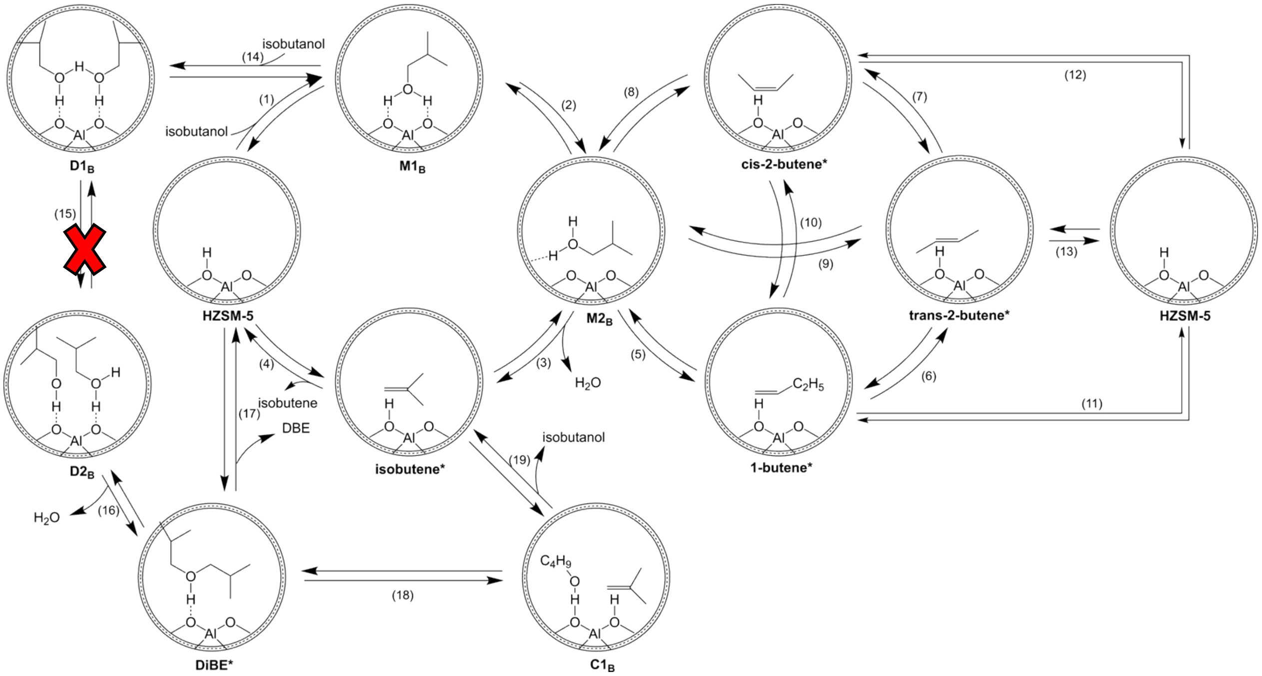

Figure S3. Proposed dehydration mechanism of isobutanol over the studied zeolites

The mechanism shown in Figure S3 for H-MFI is expected to be similar for all investigated zeolites. From $M2_B$ two transition states originate: TS1, where the β hydrogen attaches to the zeolite lattice, restoring the acid site and leading to isobutene. TS2, where there is a methyl transfer, leading to a linear butene. The activation barrier for TS1 is lower than for TS2, which leads to the higher selectivity of isobutene compared to the linear butenes. From this mechanism it is clear why the butenes are not in equilibrium: the reaction is under kinetic control. At higher temperatures, skeletal isomerization from isobutene to linear butenes and vice versa gets enabled. Under the investigated reaction conditions, the skeletal isomerization is unlikely.

All reaction steps following step 15 are expected not to occur due to the steric hindrance of the intermediates. This is based on the absence of di-isobutyl ether formation over all zeolites. Only reaction steps 1 until 14 are of importance in this mechanism.

(S5) Gibbs energies for the dehydration of n-butanol over H-MOR

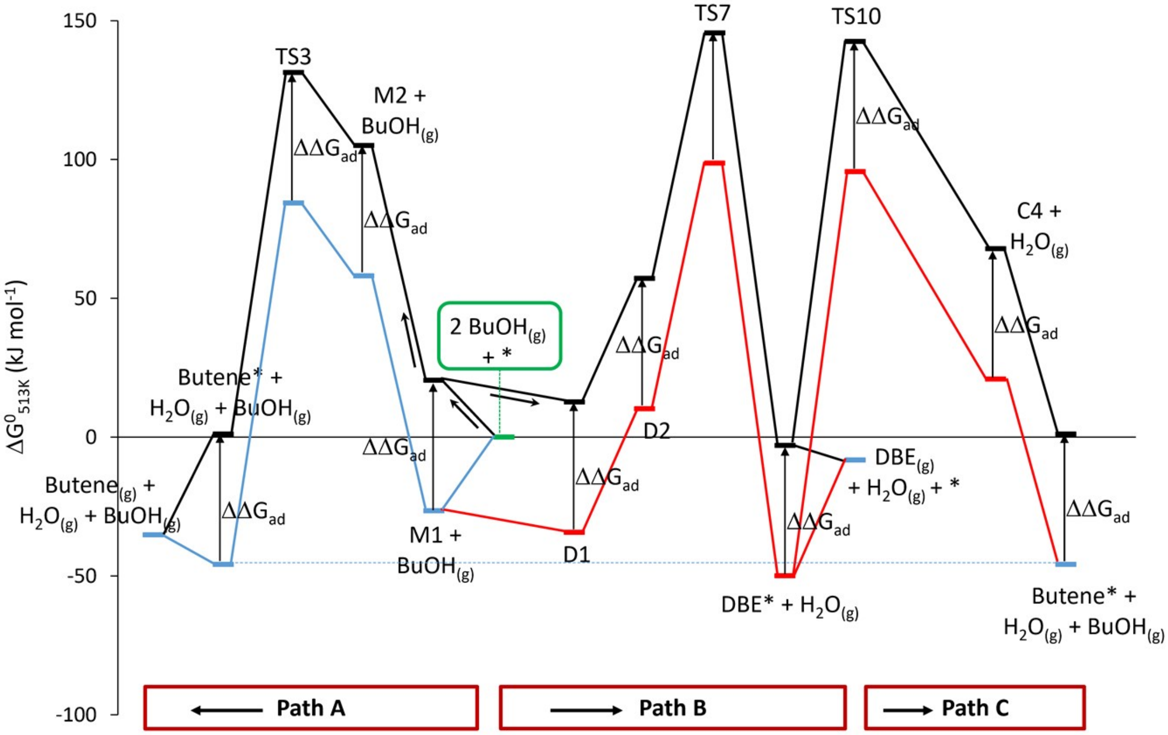

Figure S4. Visualization of the shift in Gibbs energies due to the $\Delta\Delta G_{ad}$ parameter (with $\Delta\Delta G_{ad}$ = +47 kJ mol^{-1}) on the dominant reaction mechanisms occurring for the formation of dibutyl ether (path B) and the formation of 1-butene (path A and path C) at a temperature of 513 K with as starting point H-MOR in which $\Delta\Delta G_{dis}$ is already implemented, see Figure 11 in the manuscript (blue for path A, which was not altered by implementing $\Delta\Delta G_{dis}$, and red for paths B and C, which were altered by $\Delta\Delta G_{dis}$). The final Gibbs energy profile of H-MOR in which both $\Delta\Delta G_{dis}$ and $\Delta\Delta G_{ad}$ are implemented, is shown in black. The starting point of the model is circled in green, the black arrows indicate in what direction each pathway proceeds.

Table S4: Overview of all elementary steps (n) of the n-butanol dehydration over H-MFI and H-MOR, with their kinetic parameters: Reaction Gibbs free energy (ΔG_r) and Gibbs free energy barrier ($\Delta G^{\ddagger}$) at 513 K. H-MFI free energies taken from Gunst et al. and John et al. [2-6]

n° Elementary steps	H-MFI		H-MOR	
	ΔG_r (kJ mol^{-1})	$\Delta G^{\ddagger}$ (kJ mol^{-1})	ΔG_r (kJ mol^{-1})	$\Delta G^{\ddagger}$ (kJ mol^{-1})
1 BuOH$_{(g)}$ + * ↔ M1	-26.50		20.50[a]	
2 M1 ↔ W + 1-butene$_{(g)}$	4.40	156.23	4.40	156.23
3 W ↔ $H_2O_{(g)}$ + *	-13.10		-60.10	
4 M1 ↔ C1	33.99	124.92	33.99	124.92
5 C1 ↔ W + 1-butene$_{(g)}$	-29.59		-29.59	
6 M1 ↔ M2	84.59		84.59	
7 M2 ↔ 1-butene* + $H_2O_{(g)}$	-103.97	26.29	-103.97	26.29
8 1-butene* ↔ 1-butene$_{(g)}$ + *	10.68		-36.32[a]	
9 M2 ↔ butoxy + $H_2O_{(g)}$	-62.65	34.24	-62.65	34.24
10 butoxy ↔ 1-butene*	-41.32	87.7	-41.32	87.7
11 M1 + BuOH$_{(g)}$ ↔ D1	-31.82		-7.82[b]	
12 D1 ↔ D2	44.50		44.50	
13 D2 ↔ C2 + 1-butene$_{(g)}$	-15.65	104.07	-39.65[b]	104.07
14 C2 ↔ M1 + $H_2O_{(g)}$	-32.24		-32.24	
15 D2 ↔ DBE* + $H_2O_{(g)}$	-60.15	88.44	-60.15	88.44
16 DBE* ↔ DBE$_{(g)}$ + *	65.71		-5.29[a,b]	
17 butoxy + BuOH$_{(g)}$ ↔ C3	-6.25		17.75[b]	
18 C3 ↔ DBE* (Sn2)	-63.17	66.27	-63.17	66.27
19 C3 ↔ DBE* (Sn1)	-63.17	101.81	-63.17	101.81
20 DBE* ↔ C4	70.86	145.56	70.86	145.56
21 C4 ↔ 1-butene* + BuOH$_{(g)}$	-42.76		-66.76[b]	
22 DBE* ↔ DBE2	53.38		53.38	
23 DBE2 ↔ 1-butene* + BuOH$_{(g)}$	-25.28	107.28	-49.28[b]	107.28
24 D1 ↔ C2 + trans-2-butene$_{(g)}$	22.78	136.86	-1.22[b]	136.86
25 DBE* ↔ M1 + trans-2-butene$_{(g)}$	6.20	145.94	-17.80[b]	145.94
26 1-butene* ↔ trans-2-butene*	-20.43	91.56	-20.43	91.56
27 trans-2-butene* ↔ trans-2-butene$_{(g)}$ + *	25.04		-21.96[a]	
28 1-butene* ↔ 2-butoxy	16.71	82.9	16.71	81.4
29 2-butoxy ↔ trans-2-butene*	-37.14	65.57	-37.14	65.57
30 2-butoxy ↔ cis-2-butene*	-17.26	63.07	-17.26	63.07
31 cis-2-butene* ↔ cis-2-butene$_{(g)}$ + *	7.71		-39.29[a]	
32 D1 ↔ C2 + cis-2-butene$_{(g)}$	25.34	138.86	1.34[b]	138.86
33 DBE* ↔ M1 + cis-2-butene$_{(g)}$	8.75	150.94	-15.25[b]	150.94

[a] Shift in Gibbs free energy is caused by ❒❒G_{ad}

[b] Shift in Gibbs free energy is caused by ❒❒G_{dis}

The implementation of ❒❒G_{dis} and ❒❒G_{ad} does not affect the thermodynamics, *i.e.* Gibbs energies, of gas phase reactants and products.

Table S5: Overview of all elementary steps (n) of the n-butanol dehydration over H-MFI and H-MOR, with their thermodynamic and kinetic parameters at 513 K: Reaction equilibrium constants (K) and forward rate constants (k_f). H-MFI equilibrium constants and rate constants are calculated based upon data from Gunst et al. and John et al. [2-6]

n° Elementary steps	H-MFI		H-MOR	
	K^a	k_f^b	K^a	k_f^b
1 $BuOH_{(g)}$ + * ↔ M1	4.99×10^{2}		8.18×10^{-3}	
2 M1 ↔ W + $1\text{-butene}_{(g)}$	3.56×10^{-1}	1.32×10^{-3}	3.56×10^{-1}	1.32×10^{-3}
3 W ↔ $H_2O_{(g)}$ + *	2.16×10^{1}		1.32×10^{6}	
4 M1 ↔ C1	3.46×10^{-4}	2.04×10^{0}	3.46×10^{-4}	2.04×10^{0}
5 C1 ↔ W + $1\text{-butene}_{(g)}$	1.03×10^{3}		1.03×10^{3}	
6 M1 ↔ M2	2.44×10^{-9}		2.44×10^{-9}	
7 M2 ↔ 1-butene* + $H_2O_{(g)}$	3.86×10^{10}	2.25×10^{10}	3.86×10^{10}	2.25×10^{10}
8 1-butene* ↔ $1\text{-butene}_{(g)}$ + *	8.18×10^{-2}		4.99×10^{3}	
9 M2 ↔ butoxy + $H_2O_{(g)}$	2.40×10^{6}	3.49×10^{9}	2.40×10^{6}	3.49×10^{9}
10 butoxy ↔ 1-butene*	1.61×10^{4}	1.26×10^{4}	1.61×10^{4}	1.26×10^{4}
11 M1 + $BuOH_{(g)}$ ↔ D1	1.74×10^{3}		6.26×10^{0}	
12 D1 ↔ D2	2.94×10^{-5}		2.94×10^{-5}	
13 D2 ↔ C2 + $1\text{-butene}_{(g)}$	3.92×10^{1}	2.70×10^{2}	1.09×10^{4}	2.70×10^{2}
14 C2 ↔ M1 + $H_2O_{(g)}$	1.92×10^{3}		1.92×10^{3}	
15 D2 ↔ DBE* + $H_2O_{(g)}$	1.33×10^{6}	1.06×10^{4}	1.33×10^{6}	1.06×10^{4}
16 DBE* ↔ $DBE_{(g)}$ + *	2.04×10^{-7}		3.46×10^{0}	
17 butoxy + $BuOH_{(g)}$ ↔ C3	4.33×10^{0}		1.56×10^{-2}	
18 C3 ↔ DBE* (Sn2)	2.71×10^{6}	1.91×10^{6}	2.71×10^{6}	1.91×10^{6}
19 C3 ↔ DBE* (Sn1)	2.71×10^{6}	4.59×10^{2}	2.71×10^{6}	4.59×10^{2}
20 DBE* ↔ C4	6.09×10^{-8}	1.61×10^{-2}	6.09×10^{-8}	1.61×10^{-2}
21 C4 ↔ 1-butene* + $BuOH_{(g)}$	2.26×10^{4}		6.28×10^{6}	
22 DBE* ↔ DBE2	3.67×10^{-6}		3.67×10^{-6}	
23 DBE2 ↔ 1-butene* + $BuOH_{(g)}$	3.75×10^{2}	1.27×10^{2}	1.04×10^{5}	1.27×10^{2}
24 D1 ↔ C2 + $trans\text{-2-butene}_{(g)}$	4.79×10^{-3}	1.24×10^{-1}	1.33×10^{0}	1.24×10^{-1}
25 DBE* ↔ M1 + $trans\text{-2-butene}_{(g)}$	2.34×10^{-1}	1.47×10^{-2}	6.49×10^{1}	1.47×10^{-2}
26 1-butene* ↔ trans-2-butene*	1.20×10^{2}	5.08×10^{3}	1.20×10^{2}	5.08×10^{3}
27 trans-2-butene* ↔ $trans\text{-2-butene}_{(g)}$ + *	2.82×10^{-3}		1.72×10^{2}	
28 1-butene* ↔ 2-butoxy	1.99×10^{-2}	3.87×10^{4}	1.99×10^{-2}	5.50×10^{4}
29 2-butoxy ↔ trans-2-butene*	6.05×10^{3}	2.25×10^{6}	6.05×10^{3}	2.25×10^{6}
30 2-butoxy ↔ cis-2-butene*	5.72×10^{1}	4.04×10^{6}	5.72×10^{1}	4.04×10^{6}
31 cis-2-butene* ↔ $cis\text{-2-butene}_{(g)}$ + *	1.64×10^{-1}		1.00×10^{4}	
32 D1 ↔ C2 + $cis\text{-2-butene}_{(g)}$	2.63×10^{-3}	7.75×10^{-2}	7.30×10^{-1}	7.75×10^{-2}
33 DBE* ↔ M1 + $cis\text{-2-butene}_{(g)}$	1.29×10^{-1}	4.56×10^{-3}	3.57×10^{1}	4.56×10^{-3}

[a]Calculated by $K = e^{-\frac{\Delta G_r}{RT}}$

[b]Calculated through transition state theory: $k_f = \frac{k_B T}{h} e^{(-\frac{\Delta G^{\ddagger}}{RT})}$

1. Z. Buniazet, A. Cabiac, S. Maury, D. Bianchi and S. Loridant, *Applied Catalysis B: Environmental*, 2019, **243**, 594-603.
2. M. John, K. Alexopoulos, M. F. Reyniers and G. B. Marin, *J Catal*, 2015, **330**, 28-45.
3. M. John, K. Alexopoulos, M. F. Reyniers and G. B. Marin, *ACS Catalysis*, 2016, **6**, 4081-4094.
4. M. John, K. Alexopoulos, M. F. Reyniers and G. B. Marin, *Catal Sci Technol*, 2017, **7**, 2978-2997.
5. M. John, K. Alexopoulos, M. F. Reyniers and G. B. Marin, *Catal Sci Technol*, 2017, **7**, 1055-1072.
6. D. Gunst, M. Sabbe, M.-F. Reyniers and A. Verberckmoes, *Applied Catalysis A: General*, 2019, **582**, 117101.
7. B. A. De Moor, M.-F. Reyniers, O. C. Gobin, J. A. Lercher and G. B. Marin, *The Journal of Physical Chemistry C*, 2011, **115**, 1204-1219.