Supporting Information

Investigating Reaction Mechanisms for Furfural Hydrodeoxygenation on Ni and the effect of Boron Doping on the Activity and Selectivity of the Catalyst

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S1.1 H adsorption energies

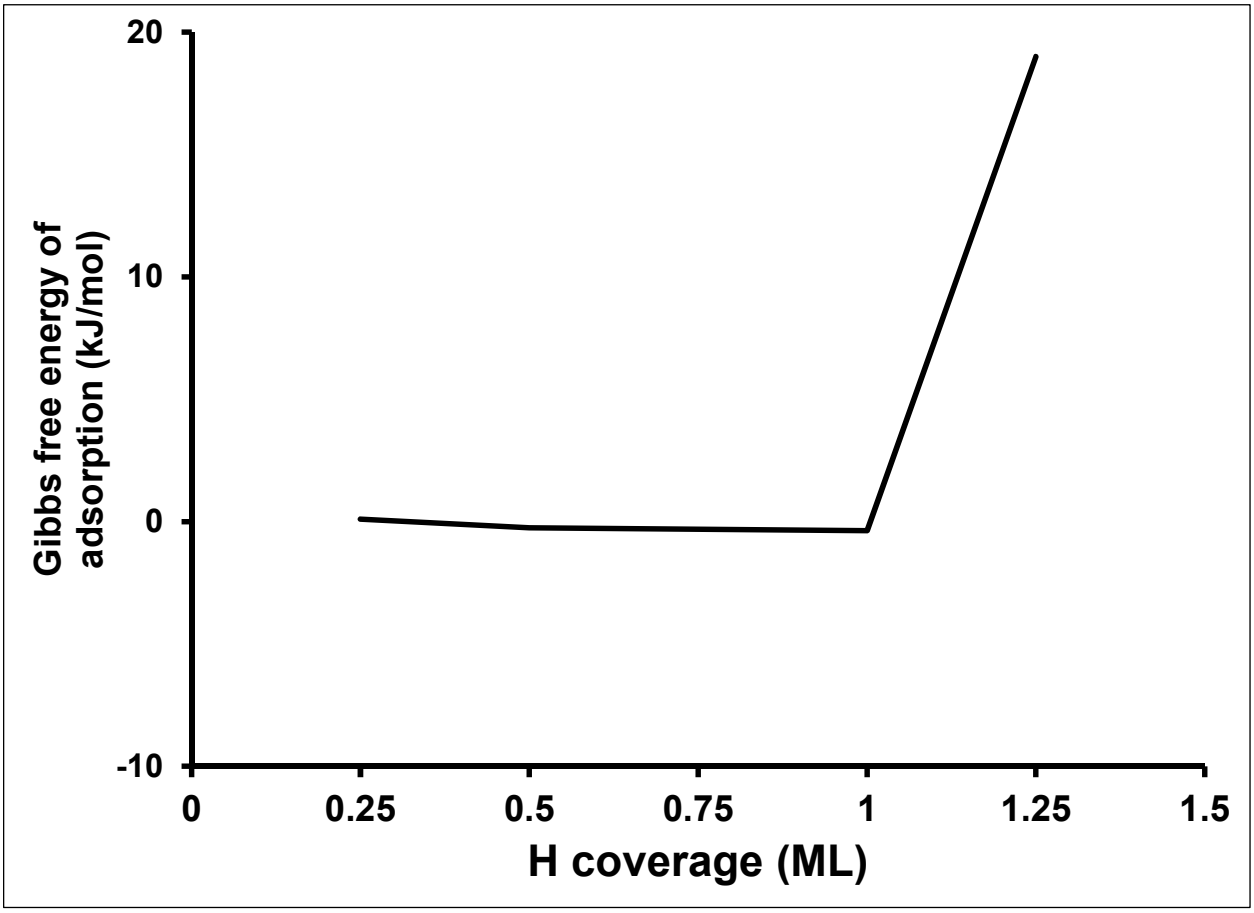
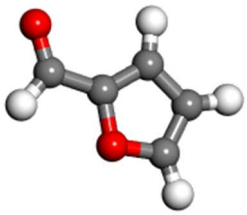
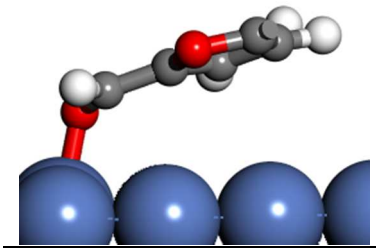


Figure S1. Effect of H coverage on the H adsorption energies on Ni(111) surfaces. H adsorbs preferentially on the fcc hollow site on Ni(111) surfaces. H coverages higher than 1 ML is not favorable.

SI. 2 Calculation of free energy of adsorption of furfural on Ni(111)

Table S1. Vibrational Frequencies of gas phase and adsorbed furfural on Ni (111) surface.

Molecule	Vibration Frequencies (cm^{-1})
	3203 3191 3175 2827 1651 1540 1437 1398 1360 1238 1144 1136 1064 1015 968 911 882 870 822 744 732 611 587 476 250 207 158
	3197 3185 3167 2913 1514 1484 1423 1377 1318 1246 1140 1132 1063 1023 903 896 882 865 822 755 725 603 576 484 315 228 200 125 98 72 64 35 9

A sample calculation for the Gibbs free energy of adsorption of furfural molecule (C_4H_3O)-CHO on Ni(111) surface at 500 K, 1 bar for a 4 layer p(4x4) unit cell having a vacuum spacing of 12 Å is shown below

$$(C_4H_3O)\text{-CHO (gas)} + * \rightarrow (C_4H_3O)\text{-CHO*}$$

Table S2 DFT calculated electronic energies, ZPE, enthalpy and entropy temperature corrections for furfural adsorption on a Ni(111) terrace.

Species	DFT calculated energy (eV)	ZPE (kJ/mol)	Enthalpy correction (kJ/mol)	Entropy Correction (J/mol K)
(C_4H_3O)-CHO (gas)	-59.36	202.6	42	385
Slab	-163.93	-	-	-
(C_4H_3O)-CHO*	-103.99	201.6	47.6	227

Reaction Enthalpy: $\Delta H_{rxn}(T)=H((C_4H_3O)\text{-CHO*}) - H((C_4H_3O)\text{-CHO})$

$$\Delta H\ (500\ K) = (-163.93 + \ 103.99 + 59.36)\ \times 96.48 + 201.6 - 202.6 + 47.6 - 42$$

$$= -51\ \text{kJ/mol}$$

$$\Delta G(500\ K) = -51 - 0.5\ \times (227 - 385)$$

$$= 28\ kJ/mol$$

Where H((C$_4$H$_3$O)-CHO) and H((C$_4$H$_3$O)-CHO*) are the enthalpies of the gas phase and adsorbed furfural respectively.

SI. 3 Convergence Studies: Effect of slab thickness, vacuum layer spacing and unit cell size on furfural binding energy

Table S3. Effect of slab thickness on the adsorption free energies (kJ/mol) of the most stable adsorption configurations of furfural at 500 K, 1 bar on a p(4x4) unit cell of Ni (111) with vaccum thickness of 12 Å. The Brillouin zone was sampled using a (3x3x1) Monkhorst Pack grid.

No. of layers	Furfural Binding Energy (kJ/mol)
3	-53
4	-57
5	-56

Table S4. Effect of vacuum spacing on the adsorption free energies of the most stable adsorption configurations of furfural at 500 K, 1 bar on a p(4x4) unit cell, 4 layer slab of Ni (111). The Brillouin zone was sampled using a (3x3x1) Monkhorst Pack grid.

Vacuum thickness	Furfural Binding Energy (kJ/mol)
12 Å	-57
15 Å	-55
20 Å	-55

Table S5. Effect of unit cell size on the adsorption free energies of the most stable adsorption configurations of furfural at 500 K, 1 bar on a 4 layer slab of Ni (111), with vaccum thickness of 12 Å. The Brillouin zone was sampled using a (3x3x1) Monkhorst Pack grid.

Unit cell size	Furfural Binding Energy (kJ/mol)
p(4 x 4)	-57
p(5 x 5)	-57
p(6 x 6)	-58

SI. 4 Reaction rates for the first step of furfural activation on H-saturated Ni surfaces

Furfural activation can take place via 6 routes on the Ni(111) surface. The rates can be defined as follows:

Rate for C^1-H cleavage $= k_1 \theta_{fur} \theta^*$ (S1)

Rate for C^5 hydrogenation $= k_2 \theta_{fur} \theta_H$ (S2)

Rate for C^1-O hydrogenation $= k_3 \theta_{fur} \theta_H$ (S3)

Rate for C^1-O cleavage $= k_4 \theta_{fur} \theta^*$ (S4)

Rate for C^1-C^2 cleavage $= k_5 \theta_{fur} \theta^*$ (S5)

Rate for ring opening (C^5-O scission) $= k_6 \theta_{fur}$ (S6)

where k_x are the rate constants of the individual reactions, θ^* is the fraction of empty sites, θ_{fur} and θ_H is the fraction of sites covered by furfural and H respectively.

Assuming a H coverage of 0.9 ML, the reaction rates for each of the above reactions can be expressed as

Rate $= K_x \theta_{fur}$ (S7)

Where K_x is the coefficient of the reaction rate for the individual reactions.

Table S6. Reaction rates for the first activation of furfural on H-saturated Ni(111) surfaces.

	Activation Barriers (kJ/mol)	**Rate constant* k (s^{-1})**	**H coverage**	**Coefficient of Reaction Rate K (s^{-1})**
C^1-H cleavage	128	0.42	0.9	**0.042**
C^5 hydrogenation	167	3.57E-05	0.9	3.21-05
C^1-O hydrogenation	135	0.078	0.9	**0.070**
C^1-O cleavage	232	5.78E-12	0.9	5.78E-13
C^1-C^2 cleavage	163	9.35E-05	0.9	9.35E-06
C^5-O scission	203	6.19E-09	0.9	6.19E-09

*pre-exponential factor of 1e13 was assumed

From Table S6, we find that the reaction rate is comparable for C^1-H cleavage and C^1-O hydrogenation and much higher than the remaining furfural activation steps. This suggests the above two steps to be the dominant furfural activation steps for the first furfural activation

SI. 5 Detailed Energetics of furfural activation on clean Ni(111), H-saturated Ni(111) and sub-surface boron doped Ni (NiB) surfaces.

Table S7. Activation energies and reaction energies (in kJ/mol) for all the studied reaction pathways for furfural activation on H-saturated Ni(111) surfaces.

	Reaction	$\Delta E_a^*/\Delta G_a$ (kJ/mol)	$\Delta E_{rxn}^*/\Delta G_{rxn}$ (kJ/mol)
	Hydrogenation Reactions		
1	(C_4H_3O)-CHO +H →(C_4H_3O)-C^1HOH	115/135	82/85
2	(C_4H_3O)-CHO +H →(C_4H_3O)-C^1H_2O	126/154	85/102
3	(C_4H_3O)-CHOH +H →(C_4H_3O)-C^1H_2OH	38/55	-32/-28
4	(C_4H_3O)-CH_2O +H →(C_4H_3O)-C^1H_2OH	77/82	-35/-43
5	(C_4H_3O)-CH_2 +H →(C_4H_3O)-C^1H_3	152/171	-15/-15
6	$C_5H_4O_2$+H → $C_4H_3O_2$ (C^5H_2)	139/167	74/104
7	$C_4H_3O_2$ (C^5H_2)+H → $C_3H_2O_2$ (C^5H_2) (C^4H_2)	132/139	38/45
8	$C_5H_3O_2$+H → $C_4H_2O_2$ (C^5H_2)	190/209	25/45
9	C_4H_3O+H → C_4H_4O (Furan)	57/54	-63/-87
10	$C_2H_2O(C^2)(C^5H_2)$ + H → C_2H_2O (C^2H)(C^5H_2)	55/54	2/3
11	$C_2H_2O(C^2H)(C^5H_2)$ +H → C_2H_2O (C^2H_2) (C^5H_2)	103/105	60/72
12	C_2H_2 (C^2H_2)(C^5H_2) + H → (C_4H) (C^2H_2)(C^5H_2) (C^3H_2)	77/77	12/14
13	(C_4H) (C^2H_2)(C^5H_2) (C^3H_2)+ H → (C^2H_2)(C^5H_2)(C^3H_2) (C^4H_2)	87/86	20/17
14	(C^2H_2)(C^5H_2)(C^3H_2) (C^4H_2)+ H → (C^2H_2)(C^5H_3)(C^3H_2) (C^4H_2)	80 /77	-60 /-71
15	(C^2H_2)(C^5H_3)(C^3H_2) (C^4H_2)+ H → C_4H_{10} (Butane)	22/9	-101/-120
16	C_2H_2O (C^2H)(C^5H_2) + H → C_2H_2 (C^2H-OH)(C^5H_2)	111/109	18/11
17	C_2H_2 (C^2H-OH)(C^5H_2) + H → C_2H_2 (C^2H_2-OH)(C^5H_2)	83/92	13/24
18	C_2H_2 (C^2H_2-OH)(C^5H_2) + H → (C^4H) (C^2H_2-OH)(C^5H_2)(C_3H_2)	100/100	45/38

19	(C^4H) $(C^2H_2\text{-}OH)(C^5H_2)(C_3H_2)$ + H → (C^4H_2) $(C^2H_2\text{-}OH)(C^5H_2)(C_3H_2)$	42 /40	-81 /-93
20	(C^4H_2) $(C^2H_2\text{-}OH)(C^5H_2)(C_3H_2)$ + H → $C_4H_{10}O$ (Butanol)	83/81	-71/-87
	C^1– O cleavage		
21	$(C_4H_3O)\text{-}CHO$ →$(C_4H_3O)\text{-}CH$ + O	197/221	65 /90
22	$(C_4H_3O)\text{-}CHOH$ →$(C_4H_3O)\text{-}CH$ + OH	205/222	137/154
23	$(C_4H_3O)\text{-}CH_2O$ →$(C_4H_3O)\text{-}CH_2$ + O	47/53	-9/-10
24	$(C^2H_2O)(C^3H)(C^5H_2)(C^4H)$→ $(C^2H_2)(C^3H)(C^5H_2)(C^4H)$+ O	81/78	-92/-100
	C – C cleavage		
25	$(C_4H_3O)\text{-}C^1HO$ →(C_4H_3O) + CHO	140/163	107/125
26	C_2H_2 $(C^5H_2)(C^2O)(C^1O)$→ C_2H_2 $(C^5H_2)(C^2O)(C^1O)$ + CO	81/106	-70/-46
27	C_2H_1O $(C^2H)(C^5H_2)(C^1O)$ → C_2H_1O $(C^2H)(C^5H_2)$+ C^1O	26/24	-136/-143
	C_{ring} – O cleavage		
28	$C_5H_4O_2$→ C_4H_4O (C^2O)	168/203	84/117
29	$C_5H_3O_2$ → $C_4H_3O(C^2O)$	114/143	43/72
30	$(C_4H_3O)\text{-}C^1HOH$→$(C_3H_3O)(C^2O)\text{-}C^1HOH$	115/145	39 /69
31	$(C_4H_3O)\text{-}C^1H_2O$→$(C_3H_3O)(C^5O)\text{-}C^1H_2O$	167/188	112/133
32	$C_4H_3O_2$ (C^5H_2) → C_3H_3O $(C^5H_2)(C^2O)$	113/113	-16/-16
	C^1 – H cleavage		
33	$C_5H_4O_2$→ $C_4H_3O_2$ + H	102/128	40/47
34	C_2H_2 $(C^5H_2)(C^2O)(C^1HO)$ → C_2H_2 $(C^5H_2)(C^2O)(C^1O)$ + H	71/75	4/8

*ΔE_a /ΔE_{rxn} and ΔG_a /ΔG_{rxn} are the electronic energy difference and Gibbs free energy change between the reactant and transition state/product at 0 K and 500 K respectively.

Table S8 Activation energies and reaction energies (in kJ/mol) for all the studied reaction pathways for furfural activation on clean Ni(111) surfaces.

	Reaction	$\Delta E_a^*/\Delta G_a$ (kJ/mol)	$\Delta E_{rxn}^*/\Delta G_{rxn}$ (kJ/mol)
	Hydrogenation Reactions		
1	(C_4H_3O)-CHO +H →(C_4H_3O)-C^1HOH	100/103	83/83
2	(C_4H_3O)-CHO +H →(C_4H_3O)-C^1H_2O	81/92	40/45
3	(C_4H_3O)-CH_2O +H →(C_4H_3O)-C^1H_2OH	90/91	-6/-16
4	(C_4H_3O)-CH_2 +H →(C_4H_3O)-C^1H_3	68/57	-24/-55
5	$C_5H_4O_2$+H → $C_4H_3O_2$ (C^5H_2)	75/95	22/44
6	$C_4H_3O_2$ (C^5H_2)+H → $C_3H_2O_2$ (C^5H_2) (C^4H_2)	103/107	59/61
7	C_4H_3O+H → C_4H_4O (Furan)	77/76	7/-21
8	$C_2H_2O(C^2)(C^5H_2)$ + H → C_2H_2O (C^2H)(C^5H_2)	78/70	10/3
9	$C_2H_2O(C^2H)(C^5H_2)$ +H → C_2H_2O (C^2H_2) (C^5H_2)	82/96	50/63
10	C_2H_2 (C^2H_2)(C^5H_2) + H → (C_4H) (C^2H_2)(C^5H_2) (C^3H_2)	54/55	9/11
11	(C_4H) (C^2H_2)(C^5H_2) (C^3H_2)+ H → (C^2H_2)(C^5H_2)(C^3H_2) (C^4H_2)	99/97	29/27
12	(C^2H_2)(C^5H_2)(C^3H_2) (C^4H_2)+ H → (C^2H_2)(C^5H_3)(C^3H_2) (C^4H_2)	75 /72	-41 /-54
13	(C^2H_2)(C^5H_3)(C^3H_2) (C^4H_2)+ H → C_4H_{10} (Butane)	50/38	-77/-97
14	C_2H_2O (C^2H)(C^5H_2) + H → C_2H_2 (C^2H-OH)(C^5H_2)	95/93	32/30
15	C_2H_2 (C^2H-OH)(C^5H_2) + H → C_2H_2 (C^2H_2-OH)(C^5H_2)	70/70	8/30
16	C_2H_2 (C^2H_2-OH)(C^5H_2) + H → (C^4H) (C^2H_2-OH)(C^5H_2)(C_3H_2)	60/37	30/20
17	(C^4H) (C^2H_2-OH)(C^5H_2)(C_3H_2) + H → (C^4H_2) (C^2H_2-OH)(C^5H_2)(C_3H_2)	81 /75	-30 /-41
18	(C^4H_2) (C^2H_2-OH)(C^5H_2)(C_3H_2) + H → $C_4H_{10}O$ (Butanol)	71/71	-78/-94

	C^1 – O cleavage		
19	(C_4H_3O)-CHO →(C_4H_3O)-CH + O	135/138	11 /20
20	(C_4H_3O)-CH_2O →(C_4H_3O)-CH_2 + O	35/47	-65/-46
21	$(C^2H_2O)(C^3H)(C^5H_2)(C^4H)$→ $(C^2H_2)(C^3H)(C^5H_2)(C^4H)$+ O	40/30	-81/-76
	C – C cleavage		
22	(C_4H_3O)-C^1HO →(C_4H_3O) + CHO	82/108	19/45
23	(C_4H_3O)-C^1O →(C_4H_3O) + C^1O	73/70	-87/-86
24	C_2H_1O $(C^2H)(C^5H_2)(C^1O)$ → C_2H_1O $(C^2H)(C^5H_2)$+ C^1O	36/32	-111/-115
	C_{ring} – O cleavage		
25	$C_5H_4O_2$→ C_4H_4O (C^2O)	58/82	-19/9
26	$C_5H_3O_2$ → $C_4H_3O(C^2O)$	87/100	-8/3
27	(C_4H_3O)-C^1H_2O→$(C_3H_3O)(C^5O)$-C^1H_2O	42/60	-40/-20
28	$C_4H_3O_2$ (C^5H_2) → C_3H_3O $(C^5H_2)(C^2O)$	74/70	-76/-76
	C^1 – H cleavage		
29	$C_5H_4O_2$→ $C_4H_3O_2$ + H	72/87	-15/1
30	C_2H_2 $(C^5H_2)(C^2O)(C^1HO)$ → C_2H_2 $(C^5H_2)(C^2O)(C^1O)$ + H	55/52	14/13

*ΔE_a /ΔE_{rxn} and ΔG_a /ΔG_{rxn} are the electronic energy difference and Gibbs free energy change between the reactant and transition state/product at 0 K and 550 K respectively.

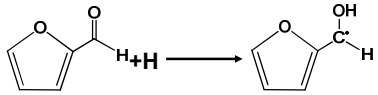
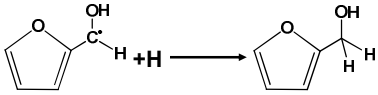
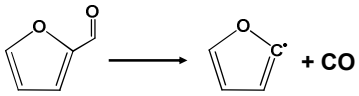
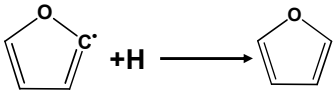
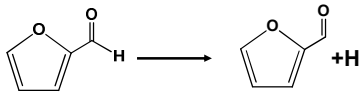
Table S9. Activation energies and reaction energies (in kJ/mol) for all the studied reaction pathways for furfural activation on sub-surface boron doped Ni surfaces.

	Reaction	$\Delta E_a^*/\Delta G_a$ (kJ/mol)	$\Delta E_{rxn}^*/\Delta G_{rxn}$ (kJ/mol)
	Hydrogenation Reactions		
1	(C_4H_3O)-CHO +H →(C_4H_3O)-C^1HOH	121/104	80/65
2	(C_4H_3O)-CHO +H →(C_4H_3O)-C^1H_2O	71/76	9/4
3	(C_4H_3O)-C^1H_2O +H →$(C_3H_2O)(C^5H_2)$-C^1H_2O	65/76	7/28
4	(C_4H_3O)-CH_2O +H →(C_4H_3O)-C^1H_2OH	80/84	17/15
5	(C_4H_3O)-CH_2 +H →(C_4H_3O)-C^1H_3	83/82	-5/-24
6	$C_5H_4O_2$+H → $C_4H_3O_2$ (C^5H_2)	58/66	9/17
7	$C_4H_3O_2$ (C^5H_2)+H → $C_3H_2O_2$ (C^5H_2) (C^4H_2)	120/117	80/76
8	C_4H_3O+H → C_4H_4O (Furan)	30/24	-37/-44
9	$C_2H_2O(C^2)(C^5H_2)$ + H → C_2H_2O (C^2H)(C^5H_2)	14/30	-30/-16
10	$C_2H_2O(C^2H)(C^5H_2)$ +H → C_2H_2O (C^2H_2) (C^5H_2)	88/88	59/55
11	$C_2H_2O(C^2H)(C^5H_2)$ +H → C_2H_2 (C^2HOH) (C^5H_2)	71/70	19/15
12	C_2H_2 (C^2H_2)(C^5H_2) + H → (C_4H) (C^2H_2)(C^5H_2) (C^3H_2)	74/75	7/8
13	(C_4H) (C^2H_2)(C^5H_2) (C^3H_2)+ H → (C^2H_2)(C^5H_2)(C^3H_2) (C^4H_2)	1/2	-70/-75
14	(C^2H_2)(C^5H_2)(C^3H_2) (C^4H_2)+ H → (C^2H_2)(C^5H_3)(C^3H_2) (C^4H_2)	65 /64	-60 /-72
15	(C^2H_2)(C^5H_3)(C^3H_2) (C^4H_2)+ H → C_4H_{10} (Butane)	17/15	-52/-68
16	C_2H_2 (C^2H-OH)(C^5H_2) + H → C_2H_2 (C^2H_2-OH)(C^5H_2)	80/83	42/45
17	C_2H_2 (C^2H_2-OH)(C^5H_2) + H → (C^4H) (C^2H_2-OH)(C^5H_2)(C_3H_2)	123/123	65/61
18	(C^4H) (C^2H_2-OH)(C^5H_2)(C_3H_2) + H → (C^4H_2) (C^2H_2-OH)(C^5H_2)(C_3H_2)	17/16	-125/-113

19	(C^4H_2) $(C^2H_2\text{-}OH)(C^5H_2)(C_3H_2)$ + H → $C_4H_{10}O$ (Butanol)	98/96	-53/-72
	C^1 – O cleavage		
20	$(C_4H_3O)\text{-}CHO$ → $(C_4H_3O)\text{-}CH + O$	189/199	77 /87
21	$(C_4H_3O)\text{-}CH_2O$ →$(C_4H_3O)\text{-}CH_2 + O$	112/119	-53/-44
22	C_2H_2 (C^2HOH) (C^5H_2) → $C_2H_2(C^2H)(C^5H_2)$ + OH	90/96	-24/-30
23	$(C_4H_3O)\text{-}C^1H_2OH$→$(C_4H_3O)\text{-}C^1H_2 + OH$	41/46	-65/-61
	C – C cleavage		
24	$(C_4H_3O)\text{-}C^1HO$ →$(C_4H_3O) + CHO$	152/154	35/36
25	$(C_4H_3O)\text{-}C^1O$ →$(C_4H_3O) + C^1O$	46/40	-62/-65
26	C_2H_1O $(C^2H)(C^5H_2)(C^1O)$ → C_2H_1O $(C^2H)(C^5H_2)$+ C^1O	45/42	-112/-123
	C_{ring} – O cleavage		
27	$C_5H_4O_2$→ C_4H_4O (C^2O)	82/90	62/60
28	$C_5H_3O_2$ → $C_4H_3O(C^2O)$	79/87	43/51
29	$(C_4H_3O)\text{-}C^1H_2O$→$(C_3H_3O)(C^5O)\text{-}C^1H_2O$	75/88	59/68
30	$(C_4H_3O)\text{-}C^1H_2$ →$(C_3H_3O)(C^2O)\text{-}C^1H_2$	55/66	37/31
31	$C_4H_3O_2$ (C^5H_2) → C_3H_3O $(C^5H_2)(C^2O)$	92/91	21/15
	C^1 – H cleavage		
32	$C_5H_4O_2$→ $C_4H_3O_2 + H$	72/69	49/51
33	C_2H_2 $(C^5H_2)(C^2O)(C^1HO)$ → C_2H_2 $(C^5H_2)(C^2O)(C^1O) + H$	35/41	25/27

*ΔE_a /ΔE_{rxn} and ΔG_a /ΔG_{rxn} are the electronic energy difference and Gibbs free energy change between the reactant and transition state/product at 0 K and 500 K respectively.

Table S10. Forces on the atoms at the transition state for selected furfural activation steps on H-saturated Ni surfaces.

Reaction	Atoms involved in bond breaking/bond forming	Calculated Forces of the atoms in X,Y and Z directions at the transition state
	O – H	O: -0.039629 0.009554 -0.001837 H: -0.026258 -0.016215 0.018665
	C^1 – H	C^1: 0.006580 0.007232 0.001532 H: 0.032841 0.006223 -0.015527
	C^1 – C^2	C^1: -0.015935 -0.014048 0.016401 C^2: -0.005229 0.009028 0.003775
	C^2 – H	C^2: -0.008966 0.028186 0.003947 H: -0.016859 0.018894 -0.022955
	C^1 – H	C^1: -0.005896 -0.030365 0.003394 H : -0.023045 -0.020052 0.046256