Elucidation of the surface structure-selectivity relationship in ethanol electro-oxidation over platinum by density functional theory

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Supporting information

1. Computational methods

DFT calculations were implemented with the Perdew-Burke-Ernzerh (PBE) generalized gradient approximation (GGA) exchange-correlation functional using the Vienna Ab-initio Simulation Package (VASP).¹⁻⁷ The projector-augmented-wave (PAW) pseudopotentials were used to describe the core electron interaction. The cut-off energy was set as 400 eV. The vacuum region layers were built more than 12 Å to ensure the slab interaction was eliminated. Microfact notation, *k*-point sampling for Brillouin zone and number of atoms for different surfaces are listed in Table S1. The bottom layer atoms were fixed in the slab while the top two layers atoms were relaxed during all the optimization process.

The transition states were located with a constrained optimization approach with the force converge criteria below 0.05 eV/Å in modified VASP.⁸⁻¹⁰ The constrained minimization technique is a much faster computational procedure for probing the potential energy surface of reactions and locating the transition state geometry. In this technique, the distance between two reacting atoms is set at a pre-selected value, which is determined by the choice of input geometry. By fixing this distance, but optimizing the geometry with respect to the remaining degrees of freedom, one can monitor the energy along the reaction coordinate by varying the constrained distance. The transition state is identified when (i) the energy along the reaction coordinate is a maximum, but a minimum with respect to all the other remaining degrees of freedom, and (ii) the forces on the atoms vanish. Furthermore, diagonalization of the Hessian matrices for sampled structures has validated that this approach yields transition states with a single imaginary eigenvalue.

In this work, the adsorption energy was defined as: $E_{ad} = E(ad/Pt) - E(ad) - E(Pt)$, where E(ad/Pt), E(ad), and E(Pt) are the total energies of the adsorbate binding to Pt surface, free adsorbate in gas phase and clean Pt, respectively. The free energy of species was obtained from G = E + ZPE + TS, where E is the total energy of species, S is the entropy and ZPE is the zero point energy at room temperature. All the vibrational frequencies, v_i (Hz), were calculated based on the harmonic oscillators approximation.¹¹ The zero point energy and entropy were calculated according to the eq 1 and 2, repectively.

$$ZPE = \sum_{i}^{hv_{i}} \frac{hv_{i}}{2}$$
(1)
$$S = R\sum_{i} \left[\frac{hv_{i}/k_{B}T}{e^{hv_{i}/k_{B}T} - 1} - ln(1 - e^{-hv_{i}/k_{B}T}) \right]$$
(2)

where h is Planck constant, k_B is Boltzmann constant and R is gas constant, T is 300

Κ.



Fig. S1 Models of platinum surfaces used in this work. The reactive step sites are highlighted by yellow.

Table S1 Microfact notation, *k*-point sampling for Brillouin zone and number of atoms for different surface models.

model	microfact notation	microfact notation k-point nur	
			atoms
(111)	/	2x2x1	48
(211)	n(111)x(100)	2x3x1	48
(511)	n(100)x(111)	3x2x1	48
(100)	/	2x2x1	48

(310)	n(100)x(110)	2x3x1	48
(320)	n(110)x(100)	2x3x1	48
(110)	/	2x2x1	64
(331)	n(111)x(110)	2x3x1	48

2. Results

2.1 Reaction mechanism, energy profiles and optimized structures

TS1: CH₃CH₂OH* \rightarrow CH₃CHOH* + H* TS2: CH₃CHOH* \rightarrow CH₂CHOH* + H* TS3: CH₂CHOH* \rightarrow CH₂COH* + H* TS4: CH₂COH* \rightarrow CH₂CO* + H* TS5: CH₂CO* \rightarrow CHCO* + H* TS6: CHCO* \rightarrow CH* + CO* TS7: CH₃CHOH* \rightarrow CH₃COH* + H* TS8: CH₃COH* \rightarrow CH₃CO* + H* TS9: CH₃CO* \rightarrow CH₂CO* + H* TS10: CH₂CO* \rightarrow CH₂* + CO* TS11: CH₂* \rightarrow CH* + H*















Fig. S2 Energy profiles for ethanol selective dehydrogenation on different surfaces. The corresponding structures are shown in Fig. S3.



































Pt(211)











TS6

TS7

TS8



Pt(511)

Pt(310)







TS9

TS10

TS11

TS12

CH₃CH₂OH* CH₃CHOH* CH₂CHOH* CH₂COH*

TS10

TS9

TS6

TS7

TS8

Pt(320)

Pt(331)

TS5

TS6

TS7

TS8

TS11

TS12

CH₃CH₂OH* CH₃CHOH* CH₂CHOH* CH₂COH*

CH₂CO*

Fig. S3 Optimized structures of transition states in ethanol electrooxidation. Blue: Pt, red: O, grey: C, white, H; yellow: stepped Pt.

surface reactions	Pt(Pt(111)		Pt(211)	
	Ea	ΔG	Ea	ΔG	
$C_2H_5OH \rightarrow C_2H_5OH^*$	/	0.28	/	0.07	
$C_2H_5OH^* \rightarrow CH_3CHOH^* + H^*$	0.50	-0.45	0.45	-0.65	
$\rm CH_3CHOH^* \rightarrow \rm CH_3COH^* + H^*$	0.65	-0.54	0.54	-0.54	
$\rm CH_3COH^* \rightarrow \rm CH_3CO^* + H^*$	0.13	-0.21	0.18	-0.72	
$CH_3CO^* \rightarrow CH_2CO^* + H^*$	0.89	-0.16	0.9	-0.09	
$\rm CH_3 CHOH^* \rightarrow \rm CH_2 CHOH^* + H^*$	0.87	-0.21	0.56	-0.40	
$\mathrm{CH_2CHOH}^* \rightarrow \mathrm{CH_2COH}^* + \mathrm{H}^*$	0.87	-0.30	0.64	-0.47	
$\mathrm{CH_2COH}^* \to \mathrm{CH_2CO}^* + \mathrm{H}^*$	0.24	-0.40	0.37	-0.48	
$CH_2CO^* \rightarrow CH_2^* + CO^*$	0.99	-0.36	0.50	-0.77	
$CH_2CO^* \rightarrow CHCO^* + H^*$	0.62	-0.22	0.88	0	
$\mathrm{CHCO}^* \to \mathrm{CH}^* + \mathrm{CO}^*$	0.68	-0.93	0.62	-1.10	
$CH_2^* \rightarrow CH^* + H^*$	0.05	-0.79	0.48	-0.33	
$CH^* \rightarrow C^* + H^*$	1.20	0.33	1.1	0.20	
surface reactions	Pt(Pt(100)		Pt(511)	
	Ea	ΔG	Ea	ΔG	
$C_2H_5OH \rightarrow C_2H_5OH^*$	/	0.28	/	0.07	
$\mathrm{C_{2}H_{5}OH^{*}} \rightarrow \mathrm{CH_{3}CHOH^{*}} + \mathrm{H^{*}}$	0.36	-0.49	0.43	-0.61	
$\rm CH_3CHOH^* \rightarrow \rm CH_3COH^* + H^*$	0.46	-0.60	0.42	-0.57	
$\rm CH_3COH^* \rightarrow \rm CH_3CO^* + H^*$	0.18	-0.47	0.16	-0.74	
$CH_3CO^* \rightarrow CH_2CO^* + H^*$	0.89	-0.04	0.95	-0.11	

0.65

-0.34

0.60

-0.48

 $CH_3CHOH^* \rightarrow CH_2CHOH^* + H^*$

Table S2 Calculated activation energies (E_a) and reaction energies (ΔG) in eV of the elementary steps on different surfaces respectively.

$CH_2CO^* \rightarrow CHCO^* + H^*$	0.47	-0.29	0.61	-0.25
$\rm CHCO^* \rightarrow \rm CH^* + \rm CO^*$	0.53	-0.67	0.64	-0.86
$CH_2^* \rightarrow CH^* + H^*$	0.98	-0.34	0.79	-0.32
$CH^* \rightarrow C^* + H^*$	0.99	-0.08	1.03	-0.07
surface reactions	Pt(110)		Pt(331)	
	Ea	ΔG	Ea	ΔΕ
$C_2H_5OH \rightarrow C_2H_5OH^*$	/	0.04	/	0.08
$C_2H_5OH^* \rightarrow CH_3CHOH^* + H^*$	0.47	-0.44	0.46	-0.44
$\mathrm{CH_3CHOH}^* \rightarrow \mathrm{CH_3COH}^* + \mathrm{H}^*$	0.47	-0.61	0.54	-0.43
$\rm CH_3COH^* \rightarrow \rm CH_3CO^* + H^*$	0.08	-0.64	0.15	-0.55
$\mathrm{CH_3CO}^* \to \mathrm{CH_2CO}^* + \mathrm{H}^*$	0.82	-0.10	0.88	0.03
$\mathrm{CH_3CHOH}^* \rightarrow \mathrm{CH_2CHOH}^* + \mathrm{H}^*$	0.33	-0.54	0.51	-0.31
$\mathrm{CH_2CHOH}^* \rightarrow \mathrm{CH_2COH}^* + \mathrm{H}^*$	0.57	-0.38	0.62	-0.28
$\mathrm{CH}_2\mathrm{COH}^* \to \mathrm{CH}_2\mathrm{CO}^* + \mathrm{H}^*$	0.27	-0.43	0.46	-0.36
$\mathrm{CH}_2\mathrm{CO}^* \to \mathrm{CH}_2^* + \mathrm{CO}^*$	0.68	-0.67	0.70	-0.62
$CH_2CO^* \rightarrow CHCO^* + H^*$	0.97	0.27	0.95	0.15
$CHCO^* \rightarrow CH^* + CO^*$	0.91	-0.95	0.56	-1.09
$CH_2^* \rightarrow CH^* + H^*$	0.77	-0.01	0.44	-0.32
$CH^* \rightarrow C^* + H^*$	0.77	0.05	1.12	0.40
surface reactions	Pt(310)		Pt(320)	
	Ea	ΔG	Ea	ΔG
$C_2H_5OH \rightarrow C_2H_5OH^*$	/	-0.11	/	-0.04
$C_2H_5OH^* \rightarrow CH_3CHOH^* + H^*$	0.54	-0.48	0.52	-0.28
$\rm CH_3CHOH^* \rightarrow \rm CH_3COH^* + H^*$	0.50	-0.67	0.44	-0.56
$CH_{3}COH^{*} \rightarrow CH_{3}CO^{*} + H^{*}$	0.16	-0.58	0.12	-0.39

$CH_2CHOH^* \rightarrow CH_2COH^* + H^*$ 0.73 -0.36 0.43 -0.47	
$CH_2COH^* \rightarrow CH_2CO^* + H^*$ 0.38 -0.41 0.35 -0.47	
$CH_2CO^* \rightarrow CH_2^* + CO^*$ 0.66 -0.62 0.48 -0.79	
$CH_2CO^* \rightarrow CHCO^* + H^*$ 0.47 -0.29 0.61 -0.25	
$CHCO^* \rightarrow CH^* + CO^*$ 0.53 -0.67 0.64 -0.86	
$CH_2^* \rightarrow CH^* + H^*$ 0.98 -0.34 0.79 -0.32	
$CH^* \rightarrow C^* + H^*$ 0.99 -0.08 1.03 -0.07	

$CH_3CO^* \rightarrow CH_2CO^* + H^*$	0.89	-0.16	0.79	-0.05
$\mathrm{CH_3CHOH}^* \rightarrow \mathrm{CH_2CHOH}^* + \mathrm{H}^*$	0.67	-0.28	0.55	-0.34
$\mathrm{CH_2CHOH}^* \to \mathrm{CH_2COH}^* + \mathrm{H}^*$	0.19	-0.82	0.42	-0.27
$\mathrm{CH_2COH}^* \rightarrow \mathrm{CH_2CO}^* + \mathrm{H}^*$	0.72	-0.31	0.22	-0.39
$\mathrm{CH}_2\mathrm{CO}^* \to \mathrm{CH}_2^* + \mathrm{CO}^*$	0.57	-0.82	0.70	-0.70
$\mathrm{CH}_2\mathrm{CO}^* \to \mathrm{CHCO}^* + \mathrm{H}^*$	0.37	-0.47	1.22	0.52
$\mathrm{CHCO}^* \to \mathrm{CH}^* + \mathrm{CO}^*$	0.77	-0.82	1.10	-1.14
$\mathrm{CH}_2^* \to \mathrm{CH}^* + \mathrm{H}^*$	0.30	-0.47	0.86	0.08
$\mathrm{CH}^* \to \mathrm{C}^* + \mathrm{H}^*$	0.73	-0.17	0.91	0.16

2.2 C-C bond breaking from CH₂CO*

Fig. S4 Calculated barriers (in eV) in $CH_2CO^* \rightarrow CHCO^*$ (blue) and $CH_2CO^* \rightarrow CH_2^* + CO^*$ (red) on different surfaces.

Fig. S5 Calculated C-C bond breaking barriers (in eV) on different surfaces.

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