Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supplementary Information

Tracing the reactivity of single atom alloys for ethanol dehydrogenation using ab initio simulations

Jayendran Iyer[1], Fatima Jalid[2], Tuhin S. Khan[3,$], M. Ali Haider[1,$]

[1]Renewable Energy and Chemicals Laboratory, Department of Chemical Engineering, Indian Institute of Technology Delhi, Hauz Khas, Delhi, 110016, India.

[2]Department of Chemical Engineering, National Institute of Technology Srinagar, Srinagar, Jammu and Kashmir, 190006, India

[3]Light Stock Processing Division, CSIR-Indian Institute of Petroleum, Dehradun, Uttarakhand, 248005, India

[$] Corresponding Authors Email: haider@iitd.ac.in, tuhins.khan@iip.res.in

Fax: +91-11-2658-2037; Tel: +91-11-26591016

Elementary reactions

The following are the elementary reactions utilized in the MKM for ethanol NODH reaction. Here, $*_s$ represents a free site (111), $*_h$ represents the hydrogen site and the gas phase species represented by (g). The superscript ^{s} and ^{h} represent species adsorbed on terrace site and hydrogen site respectively.

$$CH_3CH_2OH\ (g) + *_s \rightarrow CH_3CH_2OH_s$$

$$CH_3CH_2OH_s + *_h \leftrightarrow CH_3CH_2O\text{–}H_s + *_h \rightarrow CH_3CH_2O_s + H_h$$

$$CH_3CH_2O_s + *_h \leftrightarrow H\text{–}CH_3CHO_s + *_h \rightarrow CH_3CHO_s + H_h$$

$$CH_3CH_2OH_s + *_h \leftrightarrow CH_3CHOH\text{–}H_s + *_h \rightarrow CH_3CHOH_s + H_h$$

$$CH_3CHOH_s + *_h \leftrightarrow CH_3CHO\text{–}H_s + *_h \rightarrow CH_3CHO_s + H_h$$

$$H_h + H_h \rightarrow H\text{–}H_h + *_h \leftrightarrow H_2\ (g) + *_h + *_h$$

$$CH_3CHO_s \rightarrow CH_3CHO\ (g) + *_s$$

Table SI.1 Formation energies of the species used in the scaling MKM. These energies are referenced to CH_4, H_2O and H_2.

Species	Surface	Facet	Formation Energy (eV)
CH_3CH_2OH	None	gas	1.89
H_2	None	gas	0.00
CH_3CHO	None	gas	2.58
CO	None	gas	2.94
CH_4	None	gas	0.00
H_2O	None	gas	0.00
CH_3CH_2OH	Au	111	1.30
CH_3CH_2OH	Ag	111	1.31
CH_3CH_2OH	Pd	111	1.03
CH_3CH_2OH	Pt	111	0.96
CH_3CH_2OH	Cu	111	1.07
CH_3CH_2OH	Ni	111	0.96
CH_3CH_2OH	Rh	111	0.95
CH_3CH_2OH	Ir	111	0.91
CH_3CH_2OH	Ru	111	0.88
CH_3CH_2OH	Co	111	0.99
CH_3CH_2O	Au	111	2.43
CH_3CH_2O	Ag	111	1.73
CH_3CH_2O	Pd	111	1.39
CH_3CH_2O	Pt	111	1.73
CH_3CH_2O	Cu	111	1.00
CH_3CH_2O	Ni	111	0.72
CH_3CH_2O	Rh	111	0.94
CH_3CH_2O	Ir	111	1.37
CH_3CH_2O	Ru	111	1.04
CH_3CH_2O	Co	111	0.40
CH_3CHO	Pd	111	1.88
CH_3CHO	Pt	111	2.10
CH_3CHO	Cu	111	1.82
CH_3CHO	Ni	111	1.97
CH_3CHO	Rh	111	1.72
CH_3CH_2O-H	Au	111	3.07
CH_3CH_2O-H	Ag	111	3.05
CH_3CH_2O-H	Pd	111	2.09

CH_3CH_2O-H	Pt	111	1.80
CH_3CH_2O-H	Cu	111	2.17
CH_3CH_2O-H	Ni	111	1.84
CH_3CH_2O-H	Rh	111	1.76
CH_3CH_2O-H	Ir	111	1.68
CH_3CH_2O-H	Ru	111	1.67
CH_3CH_2O-H	Co	111	1.91
H	Ag	111	0.457
H	Pd	111	-0.45
H	Pt	111	-0.22
H	Ru	111	-0.42
H	Rh	111	-0.34
H	Fe	111	-0.56
H	Co	111	-0.48
O	Ag	111	2.56
O	Pd	111	1.45
O	Pt	111	1.80
O	Ru	111	0.01
O	Fe	111	-0.82
O	Co	111	-0.21
O	Au	111	2.64
O	Cu	111	1.15
O	Re	111	-1.15
O	Ni	111	0.44
O	Rh	111	0.84
C	Fe	111	0.49
C	Re	111	1.90
C	Co	111	1.77
C	Au	111	4.77
C	Ni	111	2.46
C	Cu	111	4.36
C	Ag	111	5.57
C	Pd	111	2.52
C	Pt	111	2.16
C	Ru	111	2.12
C	Rh	111	1.95
H-H	Pd	111	0.12
H-H	Pt	111	0.19
H-H	Cu	111	0.78
H-H	Au	111	1.15
C	NiCu	111	3.55
O	NiCu	111	0.84
C	PtCu	111	4.24

O	PtCu	111	1.46
C	PdCu	111	3.90
O	PdCu	111	1.54
C	PtAu	111	4.01
O	PtAu	111	2.29
C	NiAu	111	3.73
O	NiAu	111	1.74
C	PdAu	111	4.29
O	PdAu	111	2.45
C	PtAu	111	3.81
O	PtAu	111	2.33
C	NiAg	111	4.03
O	NiAg	111	1.34
C	PdAg	111	4.22
O	PdAg	111	2.12
C	PtAg	111	4.83
O	PtAg	111	2.25
CH_3CHOH-H	Au	111	3.25
CH_3CHOH-H	Ag	111	3.39
CH_3CHOH-H	Pd	111	1.95
CH_3CHOH-H	Pt	111	1.72
CH_3CHOH-H	Cu	111	2.70
CH_3CHOH-H	Ni	111	2.25
CH_3CHOH-H	Rh	111	2.00
CH_3CHOH-H	Ir	111	1.94
CH_3CHOH-H	Ru	111	2.21
CH_3CHOH-H	Co	111	2.34
CH_3CHO-H	Au	111	2.06
CH_3CHO-H	Ag	111	1.65
CH_3CHO-H	Pd	111	1.77
CH_3CHO-H	Pt	111	1.78
CH_3CHO-H	Cu	111	1.68
CH_3CHO-H	Ni	111	1.65
CH_3CHO-H	Rh	111	1.58
H-CH_3CHO	Au	111	2.90
H-CH_3CHO	Ag	111	2.92
H-CH_3CHO	Pd	111	2.11
H-CH_3CHO	Pt	111	2.53
H-CH_3CHO	Cu	111	2.09
H-CH_3CHO	Ni	111	2.30
H-CH_3CHO	Rh	111	1.87

CH_3CHOH	Au	111	2.83
CH_3CHOH	Ag	111	2.82
CH_3CHOH	Pd	111	1.59
CH_3CHOH	Pt	111	1.30
CH_3CHOH	Cu	111	2.32
CH_3CHOH	Ni	111	1.74
CH_3CHOH	Rh	111	1.52
CH_3CHOH	Ir	111	1.42
CH_3CHOH	Ru	111	2.11
CH_3CHOH	Co	111	1.89

Table SI.2 ML-derived E_C and E_O of Cu based SAAs

SAA Surfaces	E_C (eV)	E_O (eV)
NiCu	3.51	0.87
PtCu	3.88	1.56
PdCu	4.20	1.47

Table SI.3 Ethanol binding energy on SAA surfaces with their binding positions.

SAA surfaces	Ethanol binding on single atom B.E. (eV)	Ethanol binding on neighbouring host atom B.E. (eV)
NiCu	-0.81	-0.67
PtCu	-0.59	-0.66
PdCu	-0.67	-0.7
NiAg	-0.8	-0.51
PtAg	-0.5	-0.51
PdAg	-0.61	-0.5
NiAu	-0.91	-0.51
PtAu	-0.66	-0.49
PdAu	-0.73	-0.47

Table SI.4 Comparison of activation energy and enthalpy change of O–H activation step in route **1** on SAA surfaces with ethanol binding with comparable B.E.s on single atom and neighbouring host atom.

SAA surfaces	Ethanol binding on single atom		Ethanol binding on neighbouring host atom	
	E_a (eV)	ΔH_{rxn} (eV)	E_a (eV)	ΔH_{rxn} (eV)
PtCu	1.32	0.94	0.87	0.01
PdCu	1.38	0.2	1.06	0.15
PtAg	1.30	0.57	1.67	1.1

Table SI.5 Activation (E_a) and reaction (ΔH_{rxn}) energies of O–H and C–H activation in route **1** listed with the initial ethanol binding location.

Surfaces	Ethanol B.E. (eV)	Ethanol binding position	O–H activation		C–H activation	
			E_a (eV)	ΔH_{rxn} (eV)	E_a (eV)	ΔH_{rxn} (eV)
NiCu	-0.81	Single atom	1.03	-0.11	0.96	0.47
PtCu	-0.66	Host atom	0.87	0.008	1.02	0.41
PdCu	-0.70	Host atom	1.06	0.15	0.94	0.58
Cu	-0.74	-	1.23	0.14	1.33	0.62
NiAg	-0.79	Single atom	1.02	0.23	0.68	0.42
PtAg	-0.51	Single atom	1.30	0.57	0.33	-0.16
PdAg	-0.62	Single atom	1.39	0.59	0.74	0.17
Ag	-0.51	-	1.7	0.83	1.02	0.47
NiAu	-0.91	Single atom	1.285	0.93	0.69	0.225
PtAu	-0.66	Single atom	1.38	1.16	0.75	0.05
PdAu	-0.73	Single atom	1.355	1.50	0.43	0.15
Au	-0.52	-	1.97	1.69	0.37	-0.08

Table SI.6 Activation and reaction energies of C–H and O–H activation in route **2** listed with the initial ethanol binding at single atom center.

SAA surfaces	Ethanol B.E. (eV)	O–H activation		C–H activation	
		E_a (eV)	ΔH_{rxn} (eV)	E_a (eV)	ΔH_{rxn} (eV)
NiCu	-0.81	0.99	0.53	0.89	0.04
PtCu	-0.58	0.99	0.27	1.22	0.43
PdCu	-0.68	1.18	0.635	0.97	0.095
Cu	-0.74	1.43	1.10	0.725	-0.26
NiAg	-0.79	1.03	0.78	0.99	0.22
PtAg	-0.51	0.88	0.32	1.23	0.44
PdAg	-0.62	1.15	0.83	0.996	0.23
Ag	-0.51	1.84	1.62	0.69	-0.13
NiAu	-0.91	1.21	0.95	0.82	0.35
PtAu	-0.66	0.67	0.31	1.31	0.67
PdAu	-0.73	1.09	0.76	0.825	0.49
Au	-0.52	1.56	1.19	0.65	0.36

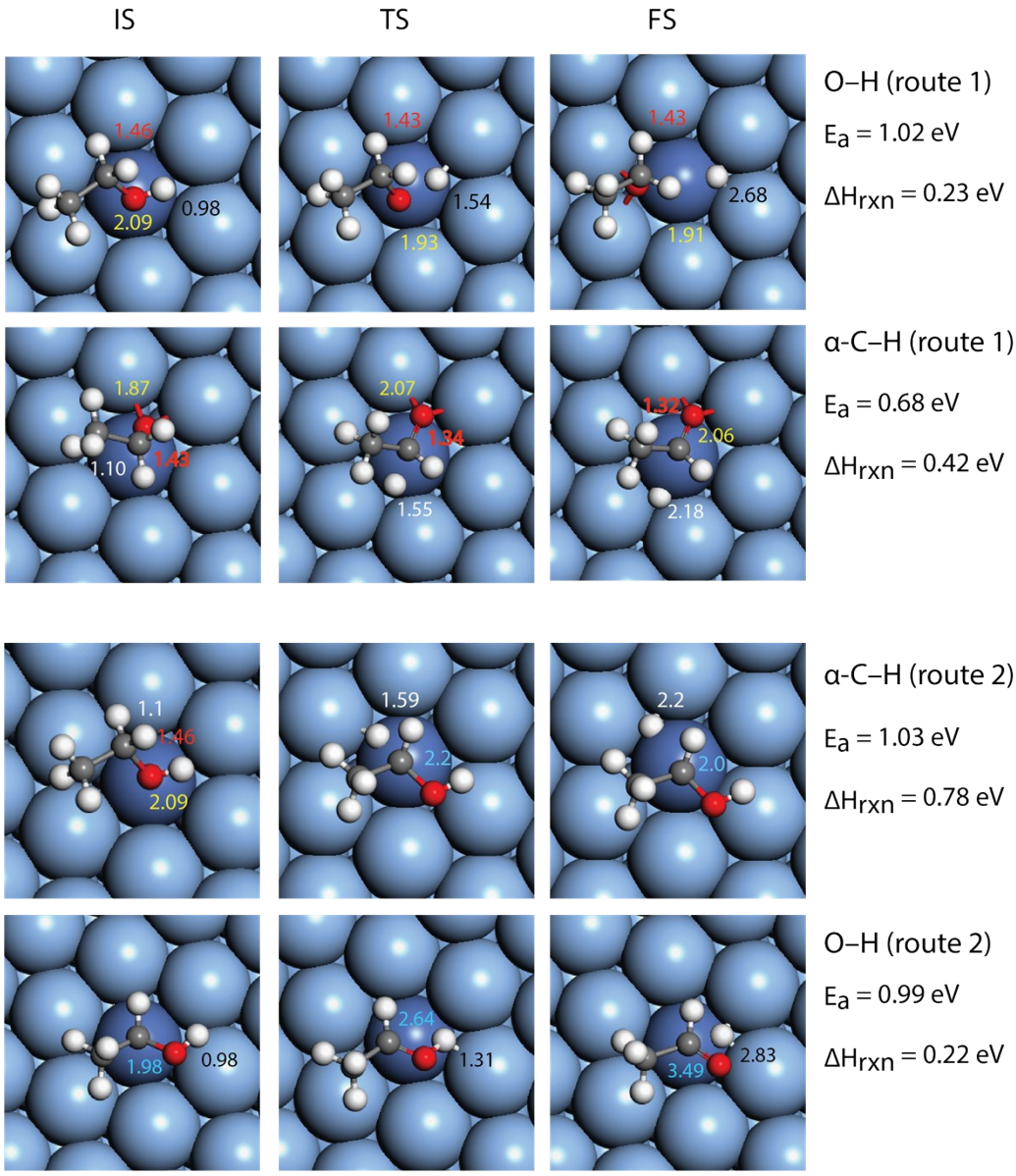

Figure SI.1 The structures of the initial (IS), transition (TS) and final (FS) state of the dehydrogenation steps in route **1** and **2** over NiAg SAA. All the energies are calculated with respect to the vapor phase energy of ethanol. The numbers in white, black, red, yellow and blue represent C–H, O–H, C–O, O–Ni and C–Ni bond distances. All the bond distances are in Å.

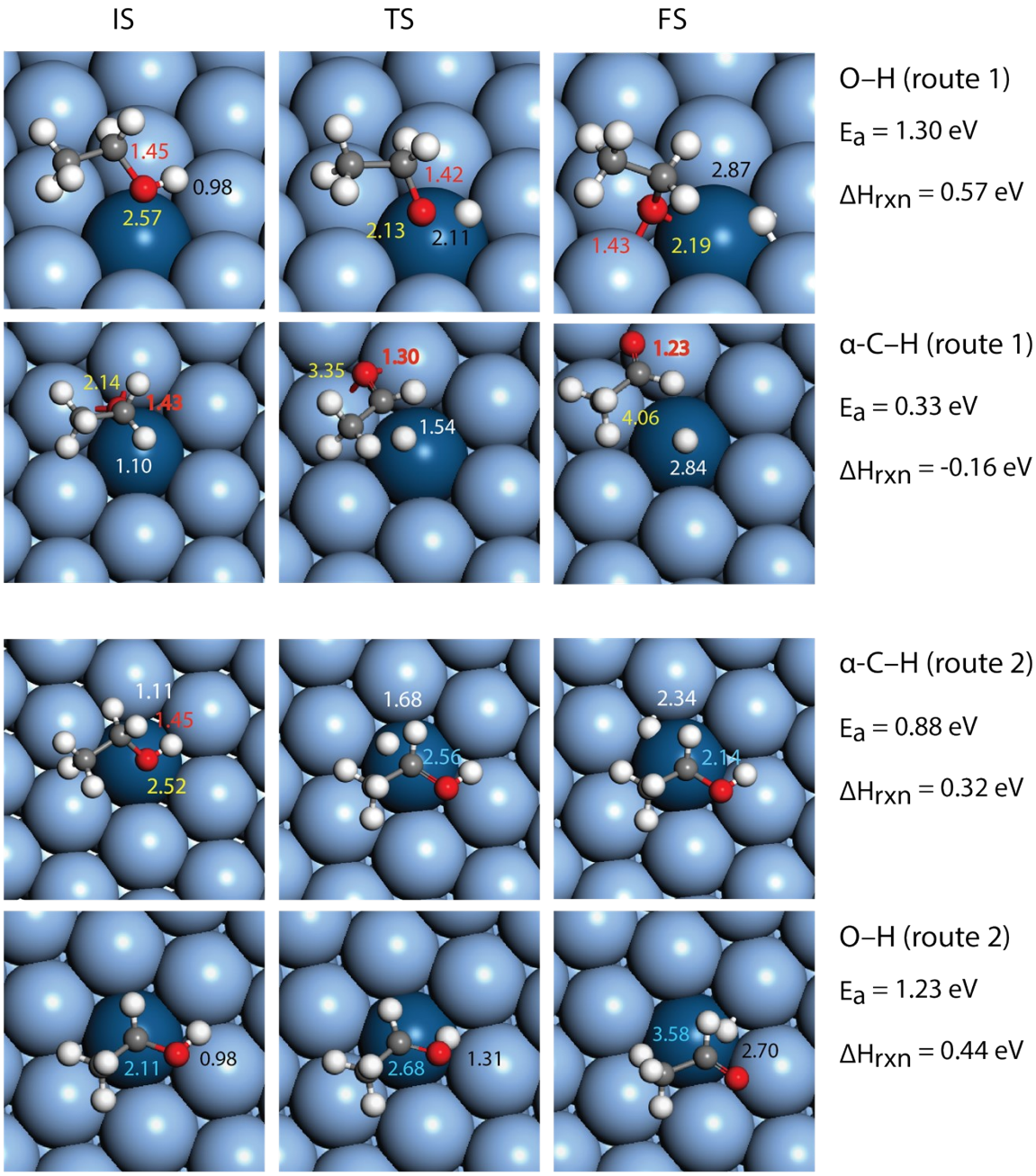

Figure SI.2 The structures of the initial (IS), transition (TS) and final (FS) state of the dehydrogenation steps in route **1** and **2** over PtAg SAA. All the energies are calculated with respect to the vapor phase energy of ethanol. The numbers in white, black, red, yellow and blue represent C–H, O–H, C–O, O–Pt and C–Pt bond distances. All the bond distances are in Å.

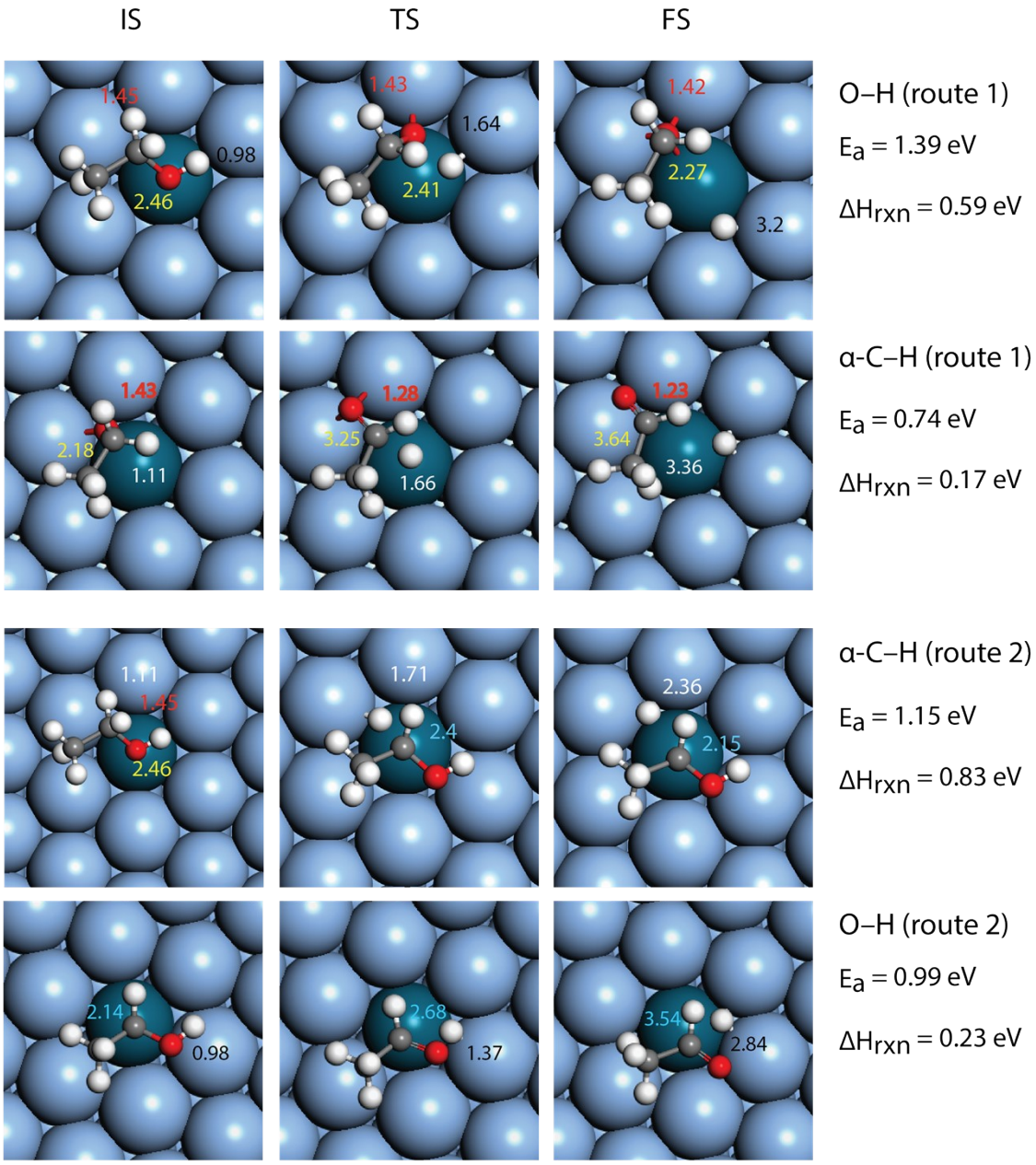

Figure SI.3 The structures of the initial (IS), transition (TS) and final (FS) state of the dehydrogenation steps in route **1** and **2** over PdAg SAA. All the energies are calculated with respect to the vapor phase energy of ethanol. The numbers in white, black, red, yellow and blue represent C–H, O–H, C–O, O–Pd and C–Pd bond distances. All the bond distances are in Å.

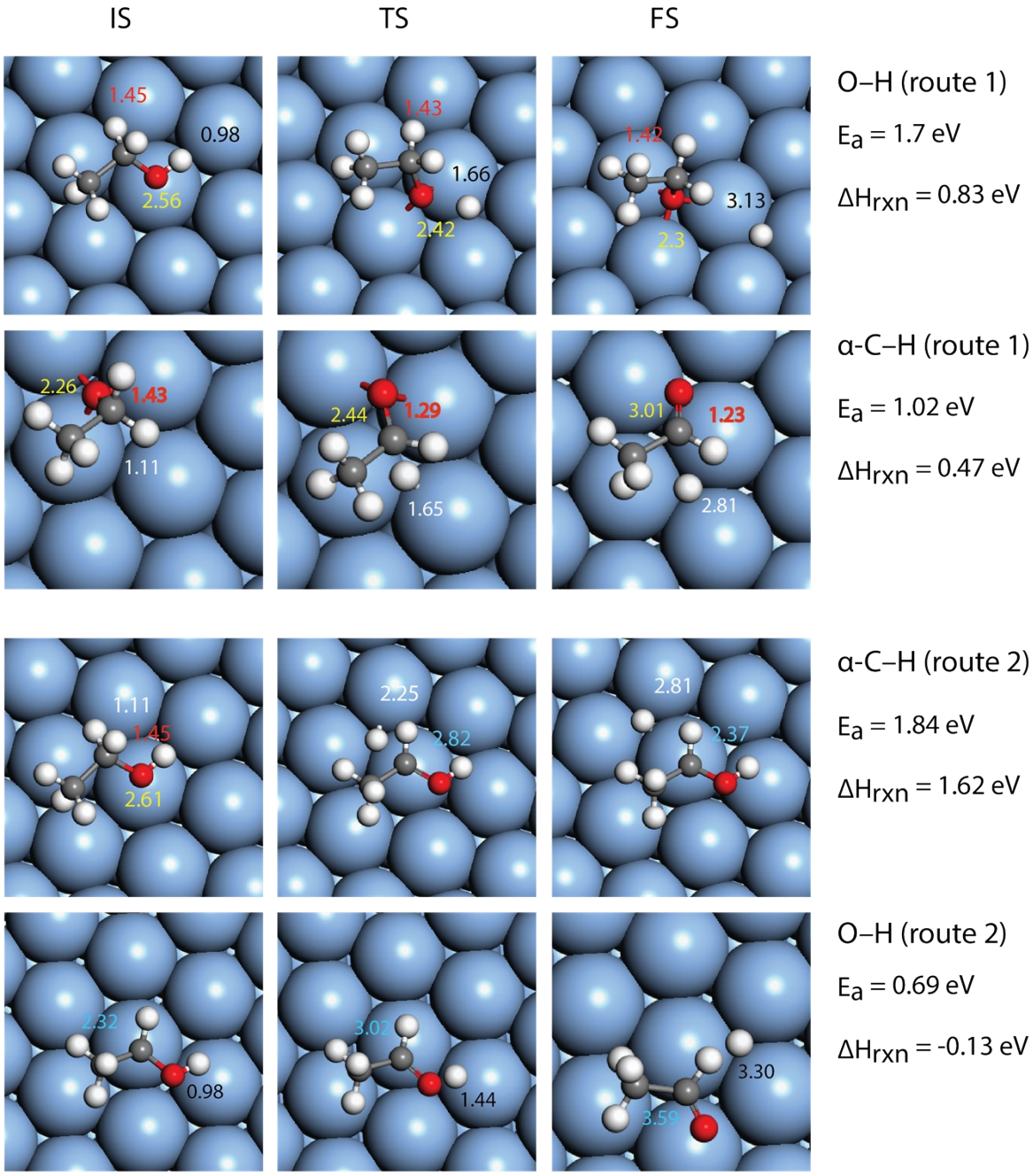

Figure SI.4 The structures of the initial (IS), transition (TS) and final (FS) state of the dehydrogenation steps in route **1** and **2** over Ag (111). All the energies are calculated with respect to the vapor phase energy of ethanol. The numbers in white, black, red, yellow and blue represent C–H, O–H, C–O, O–Ag and C–Ag bond distances. All the bond distances are in Å.

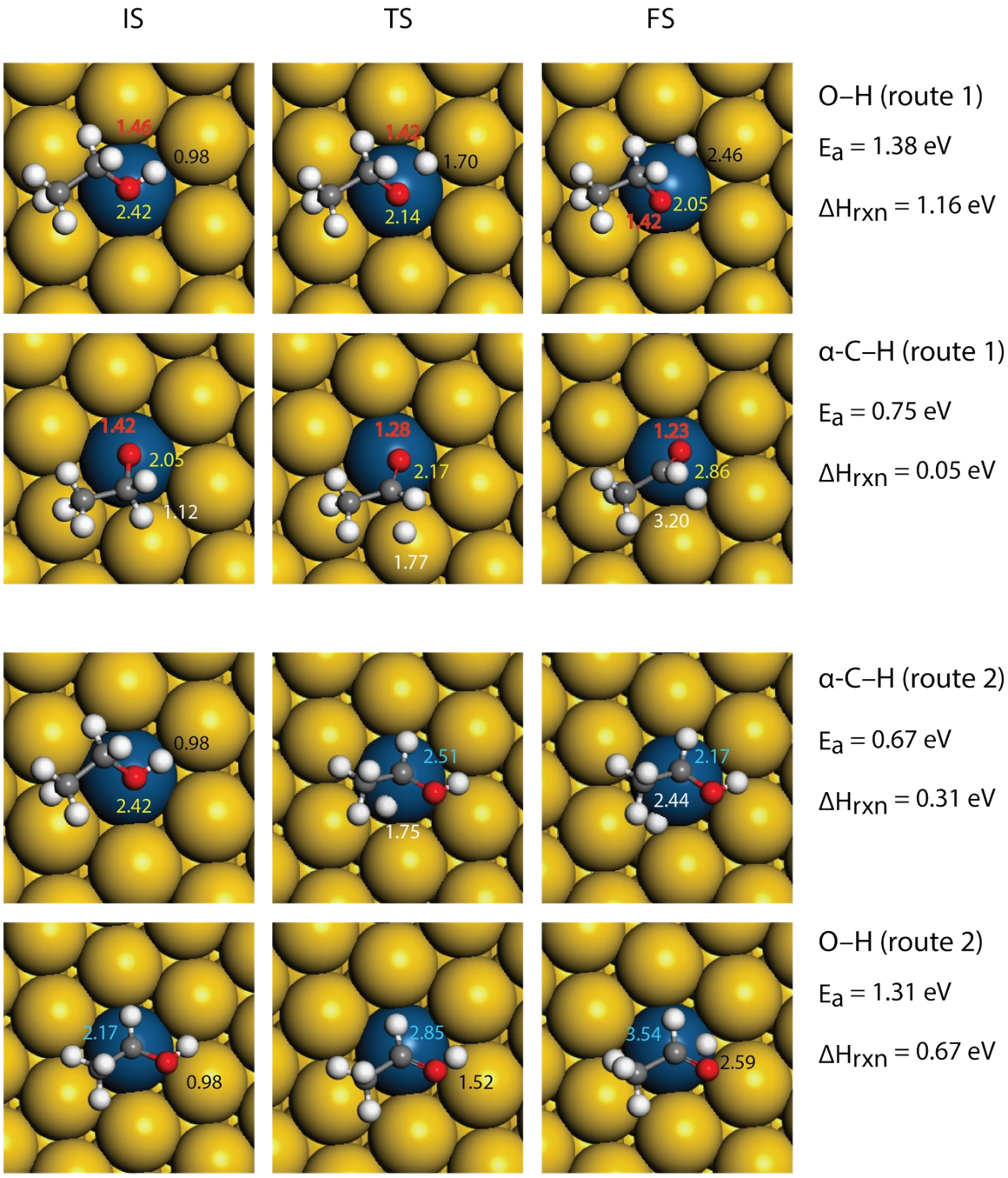

Figure SI.5 The structures of the initial (IS), transition (TS) and final (FS) state of the dehydrogenation steps in route **1** and **2** over PtAu SAA. All the energies are calculated with respect to the vapor phase energy of ethanol. The numbers in white, black, red, yellow and blue represent C–H, O–H, C–O, O–Pt and C–Pt bond distances. All the bond distances are in Å.

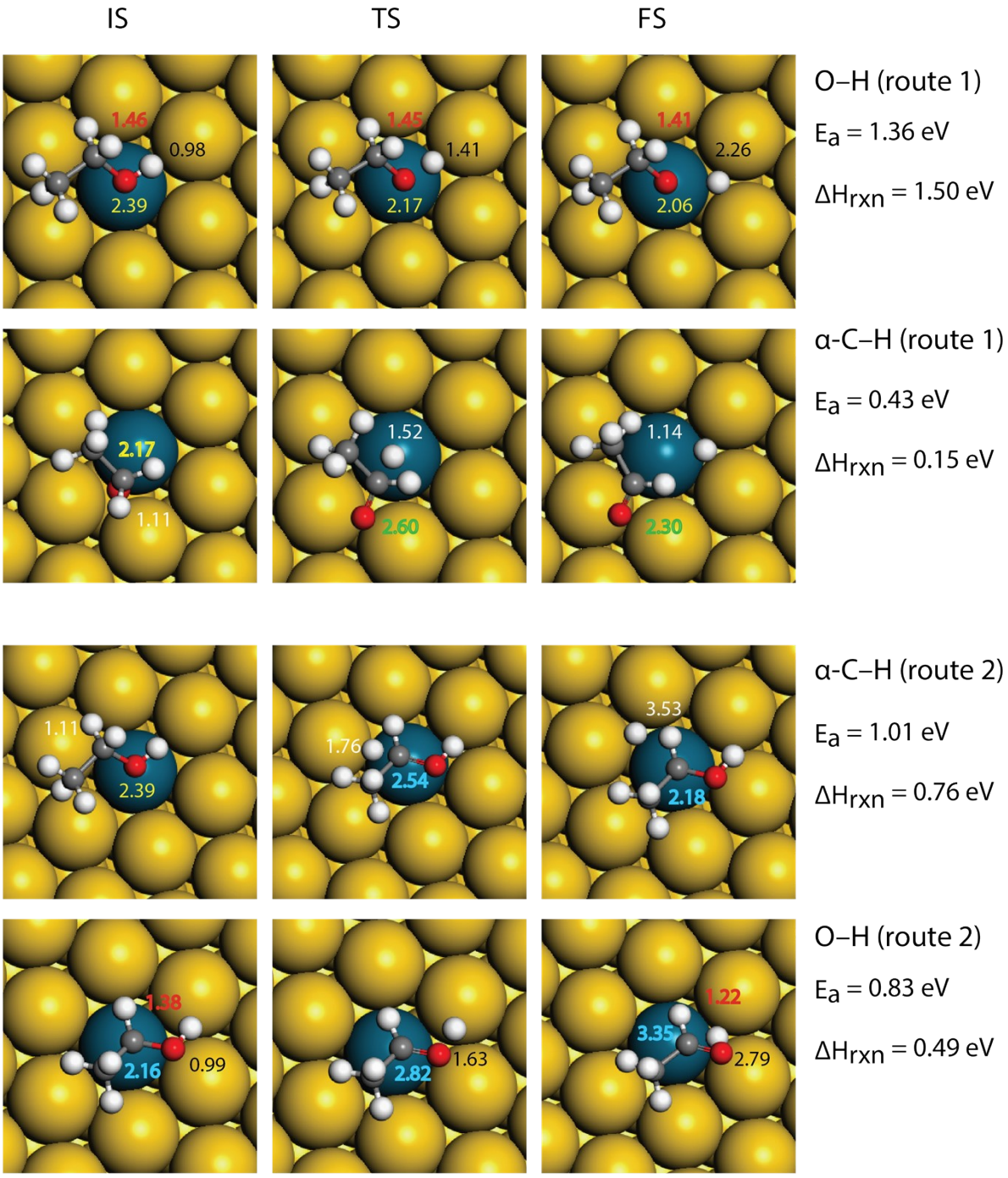

Figure SI.6 The structures of the initial (IS), transition (TS) and final (FS) state of the dehydrogenation steps in route **1** and **2** over PdAu SAA. All the energies are calculated with respect to the vapor phase energy of ethanol. The numbers in white, black, red, green, yellow and blue represent C–H, O–H, C–O, O–Au, O–Pd and C–Pd bond distances. All the bond distances are in Å.

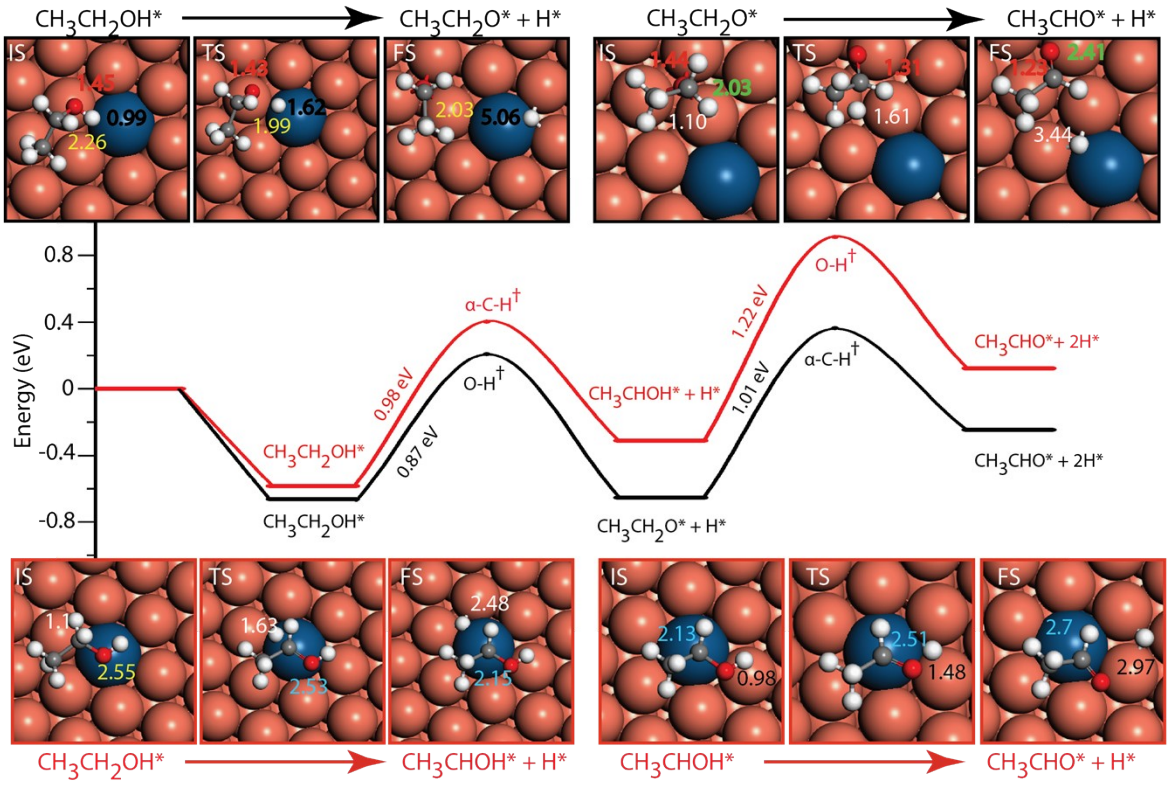

Figure SI.7 Reaction diagram for the NODH reaction on PtCu (111) via reaction route **1** (black) and route **2** (red). Images in the inset show the structures of the initial (IS), transition (TS) and final (FS) state of the elementary reaction steps. The maxima mark the TS point with the activation energy of the intrinsic step highlighted on the slope. Species represented with the * are adsorbed on the surface. All the energies are calculated with respect to the vapor phase energy of ethanol. The numbers in white, black, red, yellow, blue and green represent C–H, O–H, C–O, O–Pt, C–Pt and O–Cu bond distances. All the bond distances are in Å.

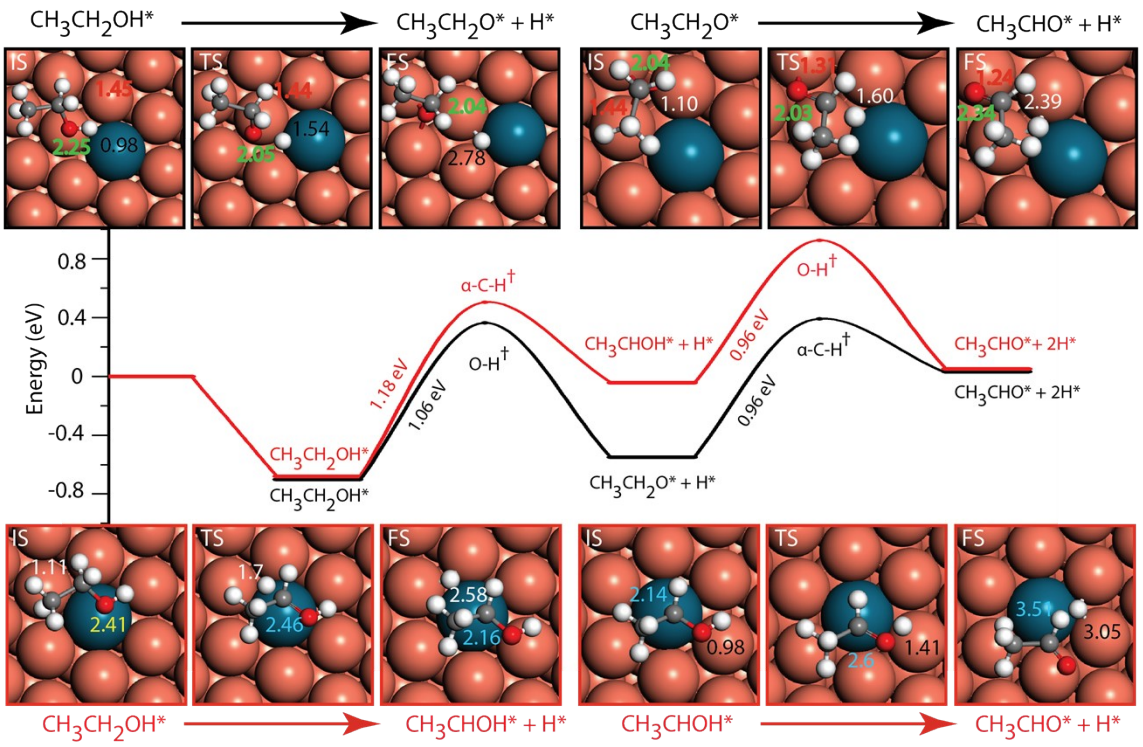

Figure SI.8 Reaction diagram for the NODH reaction on PdCu (111) via reaction route **1** (black) and route **2** (red). Images in the inset show the structures of the initial (IS), transition (TS) and final (FS) state of the elementary reaction steps. The maxima mark the TS point with the activation energy of the intrinsic step highlighted on the slope. Species represented with the * are adsorbed on the surface. All the energies are calculated with respect to the vapor phase energy of ethanol. The numbers in white, black, red, yellow, blue and green represent C–H, O–H, C–O, O–Pd, C–Pd and O–Cu bond distances. All the bond distances are in Å.