Supporting Information

Mechanistic Insights into Dominant Reaction Route and Catalyst Deactivation in Biogas Reforming using *ab initio* Microkinetic Modeling

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SI-1 Reaction Scheme

The elementary reactions included in the MKM to understand the biogas reforming (BGR) on the terrace and stepped sites of transition metal catalysts are mentioned below. '*t' represents a free step site (111), '*s' represents a free step site (211), '*h' represents the hydrogen site and the subscript '(g)' represents the gas phase species. The superscript '**t**', '**s**' and '**h**' represents species adsorbed on terrace sites, step site and hydrogen site respectively. The following are the reaction steps studied for (111) sites:

$CH_{4(g)}$ + *h + *t → CH_3^t+ H^h
$CH_{4(g)}$ + OH^t + *t → CH_3^t + H_2O^t
$CH_{4(g)}$ + O^t + *t → CH_3^t + OH^t
CH_3^t + *h → CH_2^t + H^h
CH_3^t + OH^t → CH_2^t + H_2O^t
CH_3^t + O^t → CH_2^t + OH^t
CH_2^t + *h → CH^t + H^h
CH_2^t + OH_t → CH^t + H_2O^t
CH_2^t + O^t → CH^t + OH^t
CH^t + *h → C^t + H^h
CH^t+ OH^t → C^t + H_2O^t
CH^t+ O^t → C^t + OH^t
H^h + H^h → $H_{2(g)}$ + *h + *h
O^t + H^h → OH^t + *h
O^t + H_2O^t → OH^t + OH^t
OH^t + H^h → H_2O^t + *h
H_2O^t → $H_2O_{(g)}$ + *t
C^t + O^t → CO^t + *t
CO^t → CO_g + *t
$CO_{2(g)}$ + *t + *t → CO^t + O^t

$$CO_{2(g)} + H^{h} + *t \rightarrow COOH^{t} + *h$$
$$COOH^{t} + *t \rightarrow CO^{t} + OH^{t}$$
$$C^{t} + C^{t} \rightarrow C_2^{t} + *t$$
$$C_2^{t} + C_2^{t} + C_2^{t} \rightarrow C_6^{t} + *t + *t$$
$$C_6^{t} \rightarrow C_{6\,(g)} + *t$$

The following are the reaction steps studied for (211) sites:

$$CH_{4(g)} + *h + *s \rightarrow CH_3^{s} + H^{h}$$
$$CH_{4(g)} + OH^{s} + *s \rightarrow CH_3^{s} + H_2O^{s}$$
$$CH_{4(g)} + O^{s} + *s \rightarrow CH_3^{s} + OH^{s}$$
$$CH_3^{s} + *h \rightarrow CH_2^{s} + H^{h}$$
$$CH_3^{s} + OH^{s} \rightarrow CH_2^{s} + H_2O^{s}$$
$$CH_3^{s} + O^{s} \rightarrow CH_2^{s} + OH^{s}$$
$$CH_2^{s} + *h \rightarrow CH^{s} + H^{h}$$
$$CH_2^{s} + OH\_s \rightarrow CH^{s} + H_2O^{s}$$
$$CH_2^{s} + O^{s} \rightarrow CH^{s} + OH^{s}$$
$$CH^{s} + *h \rightarrow C^{s} + H^{h}$$
$$CH^{s} + OH^{s} \rightarrow C^{s} + H_2O^{s}$$
$$CH^{s} + O^{s} \rightarrow C^{s} + OH^{s}$$
$$H^{h} + H^{h} \rightarrow H_{2(g)} + *h + *h$$
$$O^{s} + H^{h} \rightarrow OH^{s} + *h$$
$$O^{s} + H_2O\_s \rightarrow OH^{s} + OH^{s}$$
$$OH^{s} + H^{h} \rightarrow H_2O^{s} + *h$$
$$H_2O^{s} \rightarrow H_2O_{(g)} + *s$$
$$C^{s} + O^{s} \rightarrow CO^{s} + *s$$
$$CO^{s} \rightarrow CO\_g + *s$$
$$CO_{2(g)} + *s + *s \rightarrow CO^{s} + O^{s}$$
$$CO_{2(g)} + H^{h} + *s \rightarrow COOH^{s} + *h$$
$$COOH^{s} + *s \rightarrow CO^{s} + OH^{s}$$
$$C^{s} + C^{s} \rightarrow C_2^{s} + *s$$
$$C_2^{s} + C_2^{s} + C_2^{s} \rightarrow C_6^{s} + *s + *s$$
$$C_6^{s} \rightarrow C_{6\,(g)} + *s$$

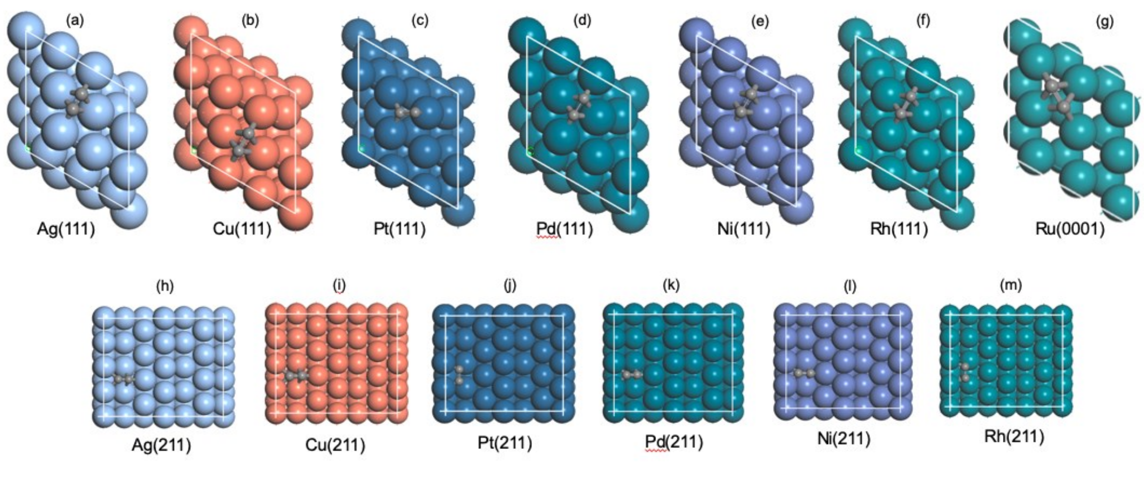

Figure SI-1 Adsorbed Configuration of C_2 on (111) and (211) facets of Ag, Cu, Pt, Pd, Ni and Rh

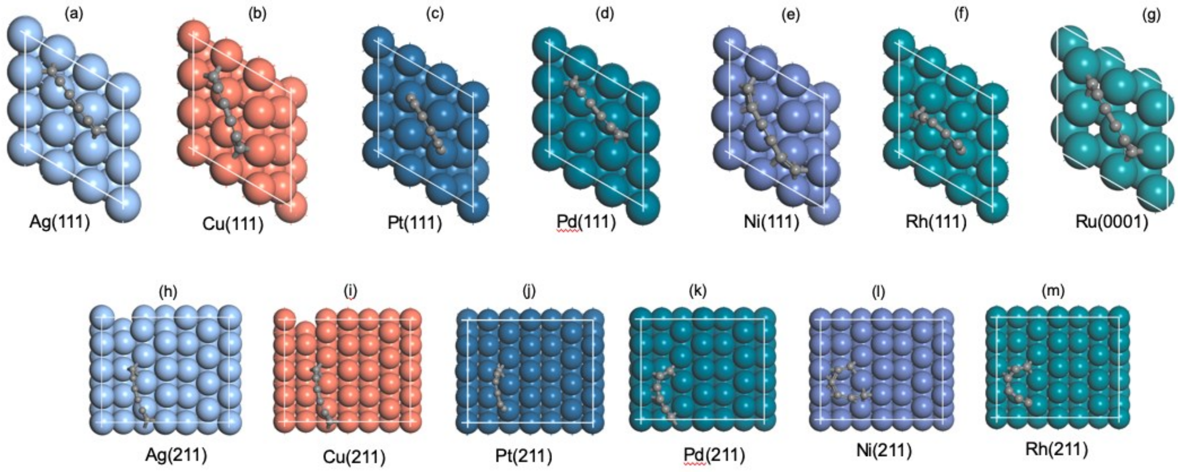

Figure SI-2 Adsorbed Configuration of C_6 on (111) and (211) facets of Ag, Cu, Pt, Pd, Ni and Rh

SI-2 Entropy and Frequency of Gas Phase Species

The fixed entropy correction for gas phase species is given in Table SI-1.

Table SI-1 Entropy of Gas Phase Species

Gas Phase Species	Entropy (eV)
H_2	0.00135
H_2O	0.0018884
CH_4	0.0018637
CO	0.0019766
CO_2	0.0021379
C_6	0.0001

The zero-point energy of the gas phase species used in the MKM are given in Table SI-2.

Table SI-2 ZPE of Gas Phase Species

Gas Phase Species	ZPE (eV)
H_2	0.54565
H_2O	0.43884, 0.1914, 0.45072
CH_4	0.35004, 0.18408, 0.18408, 0.37308, 0.37308, 0.37272, 0.37272, 0.37272
CO	0.2604
CO_2	0.15996, 0.28188, 0.08004, 0.08004
C_6	7.31736

SI-3 Reactivity of terrace sites for biogas reforming

The consumption rate of H_2, production rate of H_2O and coverage of the rest of species (O*) for MKM evaluated for BGR at terrace sites is shown in Figure SI-1, Figure SI-2 and Figure SI-3 respectively.

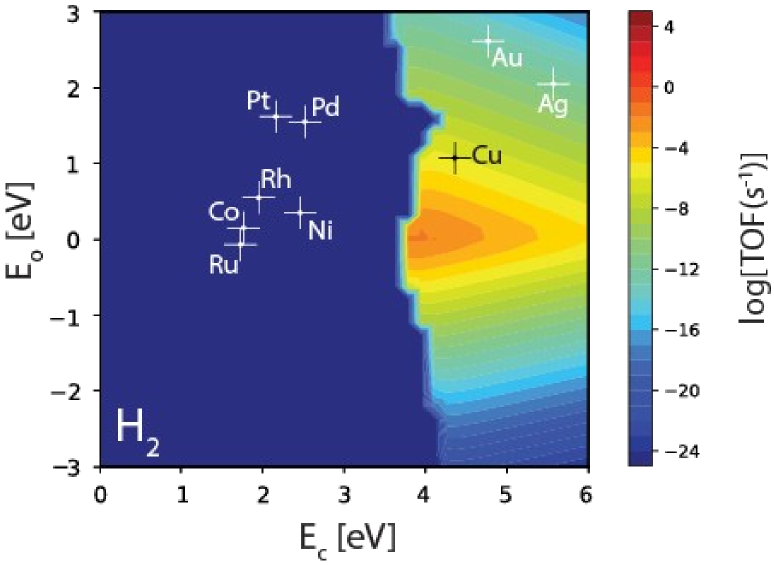

Figure SI-3 Volcano plots showing reactant consumption rates of H_2 in BGR over the (111) surfaces of transition metals. Error bar = 0.2 eV.

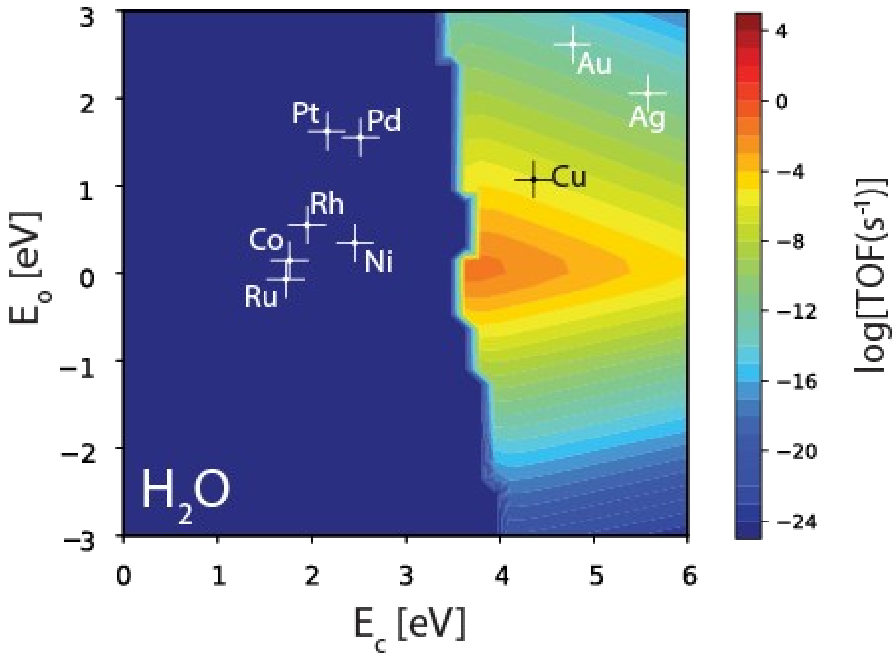

Figure SI-4 Volcano plots showing product formation rates of H_2O in BGR over the (111) surfaces of transition metals. Error bar = 0.2 eV.

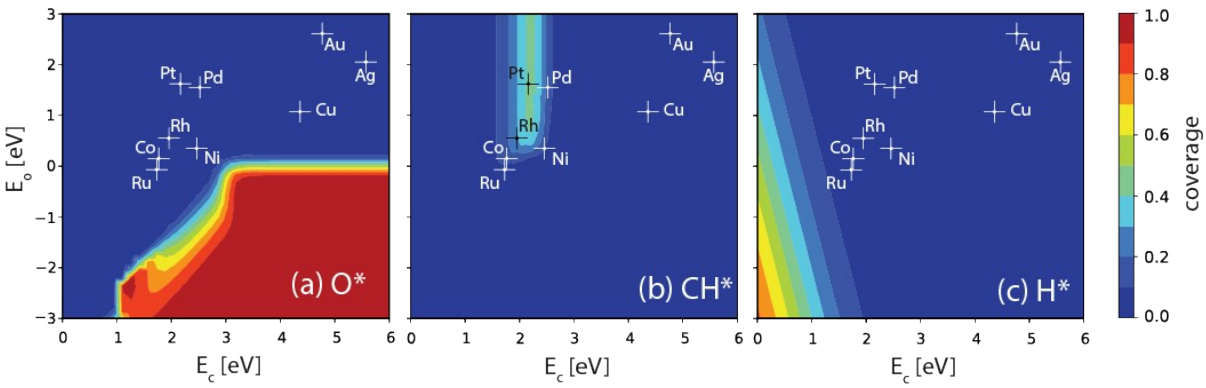

Figure SI-5 Coverage plots showing coverage of (a) O*, (b) CH* and (c) H* in BGR over the (111) surfaces of transition metals. Error bar = 0.2 eV.

SI-4 Reactivity of stepped sites for biogas reforming

The consumption rate of H_2, production rate of H_2O and coverage of the rest of species for MKM evaluated for BGR at stepped sites is shown in Figure SI-4 and Figure SI-5, respectively.

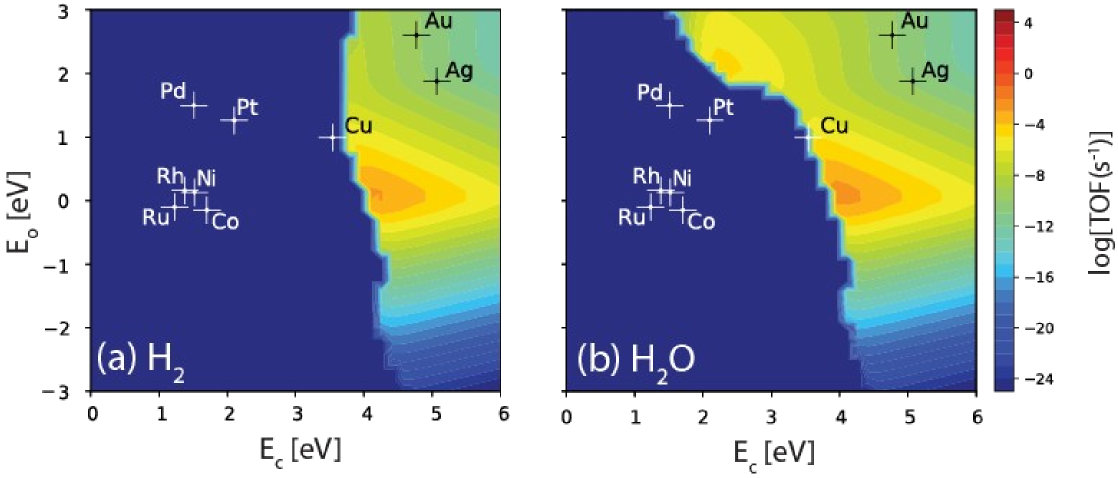

Figure SI-6 Volcano plots showing reactant consumption rate of (a) H_2 and product formation rates of (b) H_2O in BGR over the (211) surfaces of transition metals. Error bar = 0.2 eV.

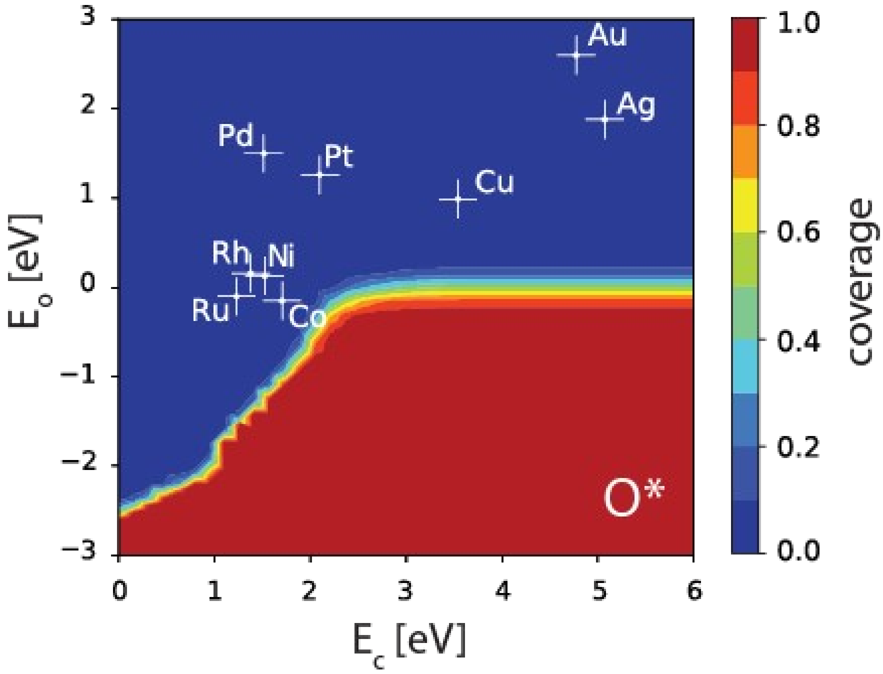

Figure SI-7 Coverage plots showing coverage of O* in BGR over the (211) surfaces of transition metals. Error bar = 0.2 eV.

SI-5 Reaction Energetics

The formation energies of the species used in the model are listed in Table SI-3. The formation energies of all the species are referenced with respect to methane, hydrogen, and water; for C, H and O atom respectively. The energies have been obtained from previous literature[1-10] and calculated in this work. The computational details of the reference articles is given in Table SI-4.

Table SI-3 Formation energies of the species used in the MKM. Formation energies are references to CH_4, H_2O and H_2.

Species	Facet	Surface	Formation Energy (eV)
CO_2	gas	None	2.47
CO	gas	None	2.77
CH_4	gas	None	0
H_2O	gas	None	0
H_2	gas	None	0
C_6	gas	None	4.66
C	111	Ag	5.57
C	111	Au	4.77
C	111	Co	1.76
C	111	Cu	4.36
C	111	Ni	2.46
C	111	Pd	2.52
C	111	Pt	2.16
C	111	Rh	1.95
C	111	Ru	1.73
C-C	111	Ag	10.97
C-C	111	Au	9.69
C-C	111	Cu	9.03
C-C	111	Ni	5.99
C-C	111	Pd	6.09
C-C	111	Pt	5.51
C-C	111	Rh	5.18
C-H	111	Ag	6.53
C-H	111	Au	5.81
C-H	111	Co	2.81
C-H	111	Cu	5.06
C-H	111	Ni	2.87
C-H	111	Pd	3.12
C-H	111	Pt	3.10
C-H	111	Rh	2.56
C-H	111	Ru	2.53
C-O	111	Ag	8.15
C-O	111	Au	7.96
C-O	111	Cu	6.40

C-O	111	Ni	4.30
C-O	111	Pd	5.31
C-O	111	Pt	5.08
C-O	111	Rh	4.05
C_2	111	Ag	6.71
C_2	111	Cu	5.72
C_2	111	Ni	4.55
C_2	111	Pd	5.28
C_2	111	Pt	5.55
C_2	111	Rh	4.45
C_2	111	Ru	3.95
C_6	111	Cu	16.84
C_6	111	Ni	15.18
C_6	111	Pd	15.51
C_6	111	Pt	16.16
C_6	111	Rh	15.96
C_6	111	Ru	14.74
CH	111	Ag	3.96
CH	111	Au	3.23
CH	111	Co	1.51
CH	111	Cu	2.85
CH	111	Ni	1.48
CH	111	Pd	1.74
CH	111	Pt	1.23
CH	111	Rh	1.21
CH	111	Ru	1.14
CH_2	111	Ag	3.04
CH_2	111	Au	2.65
CH_2	111	Co	1.45
CH_2	111	Cu	2.35
CH_2	111	Ni	1.44
CH_2	111	Pd	1.64
CH_2	111	Pt	1.21
CH_2	111	Rh	1.33
CH_2	111	Ru	1.17
CH_3	111	Ag	1.60
CH_3	111	Au	1.35
CH_3	111	Co	0.89
CH_3	111	Cu	1.30
CH_3	111	Ni	0.93
CH_3	111	Pd	0.92
CH_3	111	Pt	0.55

CH_3	111	Rh	0.84
CH_3	111	Ru	0.73
CO	111	Ag	2.99
CO	111	Au	3.04
CO	111	Cu	2.58
CO	111	Ni	1.63
CO	111	Pd	1.55
CO	111	Pt	1.70
CO	111	Rh	1.34
CO	111	Ru	1.30
CO-OH	111	Ag	4.98
CO-OH	111	Au	5.59
CO-OH	111	Cu	4.36
CO-OH	111	Ni	3.51
CO-OH	111	Pd	4.04
CO-OH	111	Pt	4.18
CO-OH	111	Rh	3.47
CO-OH	111	Ru	3.24
COO-H	111	Cu	3.79
COO-H	111	Pd	2.92
COO-H	111	Pt	3.05
COO-H	111	Rh	3.14
COOH	111	Ag	3.13
COOH	111	Au	3.01
COOH	111	Cu	2.82
COOH	111	Ni	2.25
COOH	111	Pd	2.39
COOH	111	Pt	1.41
COOH	111	Rh	1.23
H	111	Ag	0.24
H	111	Au	0.17
H	111	Cu	-0.09
H	111	Ni	-0.39
H	111	Pd	-0.40
H	111	Pt	-0.35
H	111	Rh	-0.32
H	111	Ru	-0.44
H-CH	111	Ag	4.90
H-CH	111	Au	4.26
H-CH	111	Co	1.73
H-CH	111	Cu	3.52
H-CH	111	Ni	1.78

H-CH	111	Pd	2.24
H-CH	111	Pt	1.80
H-CH	111	Rh	1.40
H-CH	111	Ru	1.39
H-CH_2	111	Ag	3.99
H-CH_2	111	Au	3.45
H-CH_2	111	Co	1.65
H-CH_2	111	Cu	2.87
H-CH_2	111	Ni	1.73
H-CH_2	111	Pd	1.95
H-CH_2	111	Pt	1.53
H-CH_2	111	Rh	1.44
H-CH_2	111	Ru	1.43
H-CH_3	111	Ag	2.49
H-CH_3	111	Au	2.23
H-CH_3	111	Co	1.43
H-CH_3	111	Cu	1.94
H-CH_3	111	Ni	1.27
H-CH_3	111	Pd	1.13
H-CH_3	111	Pt	1.06
H-CH_3	111	Rh	1.08
H-CH_3	111	Ru	1.06
H-H	111	Au	1.15
H-H	111	Cu	0.78
H-H	111	Pd	0.12
H-H	111	Pt	0.19
H-OH	111	Ag	1.78
H-OH	111	Au	2.00
H-OH	111	Co	1.03
H-OH	111	Cu	1.30
H-OH	111	Ni	0.91
H-OH	111	Pd	1.18
H-OH	111	Pt	0.85
H-OH	111	Rh	0.85
H-OH	111	Ru	0.74
H_2O	111	Ag	-0.04
H_2O	111	Au	-0.03
H_2O	111	Co	-0.05
H_2O	111	Cu	-0.04
H_2O	111	Ni	-0.05
H_2O	111	Pd	-0.08
H_2O	111	Pt	-0.05

H_2O	111	Rh	-0.11
H_2O	111	Ru	-0.21
O	111	Ag	2.05
O	111	Au	2.61
O	111	Co	0.15
O	111	Cu	1.07
O	111	Ni	0.35
O	111	Pd	1.55
O	111	Pt	1.62
O	111	Rh	0.55
O	111	Ru	-0.07
O-CO	111	Ag	5.05
O-CO	111	Au	5.74
O-CO	111	Cu	4.18
O-CO	111	Ni	3.25
O-CO	111	Pd	4.20
O-CO	111	Pt	4.04
O-CO	111	Rh	3.10
O-CO	111	Ru	2.53
O-H	111	Ag	3.09
O-H	111	Au	3.56
O-H	111	Co	1.02
O-H	111	Cu	2.03
O-H	111	Ni	1.18
O-H	111	Pd	2.12
O-H	111	Pt	2.12
O-H	111	Rh	1.52
O-H	111	Ru	1.31
OH	111	Ag	0.67
OH	111	Au	1.39
OH	111	Co	0.05
OH	111	Cu	0.30
OH	111	Ni	0.20
OH	111	Pd	0.94
OH	111	Pt	0.96
OH	111	Rh	0.43
OH	111	Ru	0.19
C	211	Ag	5.07
C	211	Au	4.77
C	211	Co	1.70
C	211	Cu	3.54
C	211	Ni	1.52

C	211	Pd	1.51
C	211	Pt	2.10
C	211	Rh	1.38
C	211	Ru	1.23
C-C	211	Ag	11.02
C-C	211	Au	10.36
C-C	211	Co	5.07
C-C	211	Cu	8.22
C-C	211	Pt	6.03
C-C	211	Rh	4.51
C-C	211	Ru	4.37
C-H	211	Cu	4.31
C-H	211	Pd	2.25
C-H	211	Pt	3.06
C-H	211	Rh	1.97
C-H	211	Ru	1.74
C-HO	211	Ag	5.92
C-HO	211	Cu	4.15
C-HO	211	Pd	2.73
C-HO	211	Pt	3.26
C-HO	211	Rh	2.01
C-HOH	211	Ag	5.40
C-HOH	211	Cu	4.03
C-HOH	211	Pd	2.29
C-HOH	211	Pt	2.83
C-HOH	211	Rh	2.08
C-O	211	Ag	8.07
C-O	211	Au	8.18
C-O	211	Co	3.19
C-O	211	Ni	3.43
C-O	211	Pd	4.63
C-O	211	Pt	4.11
C-O	211	Rh	3.03
C-O	211	Ru	2.80
C_2	211	Ag	5.8
C_2	211	Cu	4.44
C_2	211	Ni	3.57
C_2	211	Pd	4.03
C_2	211	Rh	4.23
C_6	211	Ag	16.63
C_6	211	Cu	15.28
C_6	211	Ni	14.13

C_6	211	Pd	13.44
C_6	211	Pt	14.28
C_6	211	Rh	12.22
CH	211	Ag	3.96
CH	211	Au	3.43
CH	211	Co	1.16
CH	211	Cu	2.70
CH	211	Ni	1.22
CH	211	Pd	1.57
CH	211	Pt	1.19
CH	211	Rh	1.01
CH	211	Ru	0.71
CH_2	211	Ag	2.87
CH_2	211	Au	2.23
CH_2	211	Co	0.79
CH_2	211	Cu	2.22
CH_2	211	Ni	1.14
CH_2	211	Pd	1.28
CH_2	211	Pt	0.76
CH_2	211	Rh	0.76
CH_2	211	Ru	0.69
CH_3	211	Ag	1.39
CH_3	211	Au	1.10
CH_3	211	Co	0.04
CH_3	211	Cu	0.97
CH_3	211	Ni	0.39
CH_3	211	Pd	0.79
CH_3	211	Pt	0.46
CH_3	211	Rh	0.36
CH_3	211	Ru	0.06
CO	211	Ag	2.87
CO	211	Au	2.57
CO	211	Co	1.40
CO	211	Cu	2.28
CO	211	Ni	1.25
CO	211	Pd	1.22
CO	211	Pt	1.11
CO	211	Rh	1.07
CO	211	Ru	0.98
CO-OH	211	Ag	3.75
CO-OH	211	Au	4.14
CO-OH	211	Cu	2.97

CO-OH	211	Pd	3.10
CO-OH	211	Pt	2.80
CO-OH	211	Rh	2.40
CO-OH	211	Ru	2.27
COO-H	211	Ag	4.36
COO-H	211	Cu	3.88
COO-H	211	Pd	2.85
COO-H	211	Pt	2.62
COO-H	211	Rh	2.60
COOH	211	Ag	3.05
COOH	211	Cu	2.70
COOH	211	Pd	2.17
COOH	211	Pt	1.94
COOH	211	Rh	1.59
H	211	Ag	0.24
H	211	Au	0.17
H	211	Cu	-0.09
H	211	Ni	-0.39
H	211	Pd	-0.40
H	211	Pt	-0.35
H	211	Rh	-0.32
H	211	Ru	-0.44
H-CH	211	Ag	4.74
H-CH	211	Au	4.58
H-CH	211	Co	1.78
H-CH	211	Cu	3.27
H-CH	211	Ni	1.93
H-CH	211	Pd	2.05
H-CH	211	Pt	2.35
H-CH	211	Rh	1.54
H-CH	211	Ru	1.07
H-CH_2	211	Ag	3.52
H-CH_2	211	Au	2.81
H-CH_2	211	Co	0.99
H-CH_2	211	Cu	2.50
H-CH_2	211	Ni	1.41
H-CH_2	211	Pd	1.53
H-CH_2	211	Pt	0.94
H-CH_2	211	Rh	0.79
H-CH_2	211	Ru	0.68
H-CH_3	211	Ag	2.23
H-CH_3	211	Au	1.83

H-CH_3	211	Co	0.86
H-CH_3	211	Cu	1.70
H-CH_3	211	Ni	1.13
H-CH_3	211	Pd	0.83
H-CH_3	211	Pt	0.73
H-CH_3	211	Rh	0.66
H-CH_3	211	Ru	0.52
H-H	211	Au	1.15
H-H	211	Cu	0.78
H-H	211	Pd	0.12
H-H	211	Pt	0.19
H-OH	211	Au	1.82
H-OH	211	Cu	0.80
H-OH	211	Ni	0.35
H-OH	211	Pd	0.82
H-OH	211	Pt	0.72
H-OH	211	Rh	0.49
H-OH	211	Ru	-0.01
H_2O	211	Ag	-0.12
H_2O	211	Co	-0.37
H_2O	211	Cu	-0.18
H_2O	211	Ni	-0.32
H_2O	211	Pd	-0.18
H_2O	211	Pt	-0.14
H_2O	211	Rh	-0.29
H_2O	211	Ru	-0.57
HOH-CH	211	Ag	4.44
HOH-CH	211	Cu	3.30
HOH-CH	211	Pd	2.34
HOH-CH	211	Pt	2.04
HOH-CH	211	Rh	1.76
HOH-CH_2	211	Ag	3.51
HOH-CH_2	211	Cu	2.89
HOH-CH_2	211	Pd	2.09
HOH-CH_2	211	Pt	1.67
HOH-CH_2	211	Rh	1.55
HOH-CH_3	211	Ag	2.23
HOH-CH_3	211	Cu	1.82
HOH-CH_3	211	Pd	1.67
HOH-CH_3	211	Pt	1.42
HOH-CH_3	211	Rh	1.20
O	211	Ag	1.88

O	211	Au	2.60
O	211	Co	-0.15
O	211	Cu	0.99
O	211	Ni	0.13
O	211	Pd	1.50
O	211	Pt	1.26
O	211	Rh	0.16
O	211	Ru	-0.10
O-CO	211	Ag	5.10
O-CO	211	Au	5.45
O-CO	211	Co	2.73
O-CO	211	Cu	3.92
O-CO	211	Ni	2.77
O-CO	211	Pd	3.99
O-CO	211	Pt	3.53
O-CO	211	Rh	2.56
O-CO	211	Ru	2.35
O-H	211	Ag	2.80
O-H	211	Au	3.18
O-H	211	Cu	1.63
O-H	211	Ni	0.68
O-H	211	Pd	1.75
O-H	211	Pt	1.60
O-H	211	Rh	0.73
O-H	211	Ru	0.27
O-HOH	211	Ag	2.65
O-HOH	211	Cu	1.83
O-HOH	211	Pd	2.28
O-HOH	211	Pt	2.10
O-HOH	211	Rh	1.03
OH	211	Ag	0.49
OH	211	Au	0.94
OH	211	Cu	-0.04
OH	211	Ni	-0.50
OH	211	Pd	0.34
OH	211	Pt	0.36
OH	211	Rh	-0.37
OH	211	Ru	-0.69
OH-CH	211	Ag	4.97
OH-CH	211	Cu	3.43
OH-CH	211	Pd	2.78
OH-CH	211	Pt	2.47

OH-CH	211	Rh	1.69
$OH-CH_2$	211	Ag	4.03
$OH-CH_2$	211	Cu	3.01
$OH-CH_2$	211	Pd	2.53
$OH-CH_2$	211	Pt	2.10
$OH-CH_2$	211	Rh	1.48
$OH-CH_3$	211	Ag	2.76
$OH-CH_3$	211	Cu	1.94
$OH-CH_3$	211	Pd	2.11
$OH-CH_3$	211	Pt	1.85
$OH-CH_3$	211	Rh	1.13
OH-OH	211	Ag	1.98
OH-OH	211	Cu	1.07
OH-OH	211	Pd	1.72
OH-OH	211	Pt	1.76
OH-OH	211	Rh	0.50

Table SI-4 Computational details of the reference used for CatMAP data

Reference	Article	DFT Method	XC	Potential	Slab Size
1.	*Energy Environ. Sci.* 3, 1311–1315 (2010)	DACAPO	RPBE	USPP	3×2×3 and 3 x 3 x 3 depending upon the adsorbate size
2.	*Top Catal.* 57, 135–142 (2014)	DACAPO	RPBE	USPP	3 x 1 for (211)
3.	*Phy. Rev. Lett.* 99, 016105 (2007)	DACAPO	RPBE	USPP	2 x 2 for 111 1 x 2 for 211
4.	*Phys. Chem. Chem. Phys*. 13, 20760–20765 (2011)	DACAPO	RPBE	USPP	2 x 2 for (111) 1 x 2, 2 x 2, and 2 x 3 for (211) surfaces depending on the size of the adsorbed molecules.
5.	*J. Phys. Chem. C* 113, 10548–10553 (2009)	DACAPO	RPBE	USPP	2 x 2 for (111) 2 x 1 for (211)
6.	*Angew. Chem. Int. Ed*. 47, 4835 – 4839 (2008)	DACAPO	RPBE	USPP	2 x 2 for (111) surface
7.	*Catal. Lett*. 141, 370–373 (2011)	DACAPO	RPBE	USPP	1 x 2 for (211)
8.	*J. Catal,* 293, 51–60 (2012)	DACAPO	RPBE	USPP	1 x 3 for (211)
10.	*J Catal*. 374, 161–	Quantum	BEEF-	GBRV	3 x 2 for (111)

	170 (2019).	Espresso	vdW		
12.	*Top Catal 57, 80–88 (2014).*	DACAPO	RPBE	USPP	2 x 2 for (111) 2 x 1 for (211)
13.	*J. Am. Chem. Soc.* 133, 5009–5015 (2007).	VASP	PW91	USPP	The metal slab for (111) with appropriate size with the supercell size was fixed during the optimization of the C clusters

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