Supporting Information:

Investigating the Innate Selectivity Issues of Methane to Methanol: Consideration of an Aqueous Environment

Rhys J. Bunting, Peter S. Rice, Jillian Thompson, P. Hu*

School of Chemistry and Chemical Engineering, Queen's University Belfast, David Keir Building, Stranmillis Road, Belfast, BT9 5AG

Corresponding Author:

*p.hu@qub.ac.uk

Contents of Supporting Information:

Discrete energies for C-H activation, C-O coupling, and C-OH coupling for a variety of fcc metals – SI1

Tabularised form of the free energies calculated by umbrella sampling for the Pd(111) surface – SI2

Energies of additional elementary steps considered for the Pd(111) surface – SI3

C-O coupling in the aqueous phase snapshot – SI4

SI1: Total energy changes and total energy barriers for the elementary steps of C-H activation, C-O coupling, and C-OH coupling for a variety of fcc metal surfaces. All energies are in eV.

C-H	CH3-H		CH2OH-H	
Metal	ΔU (eV)	Ea (eV)	ΔU (eV)	Ea (eV)
Ag	1.74	2.251	1.491	1.844
Au	1.303	1.848	0.926	1.509
Cu	0.902	1.577	0.716	1.272
Ir	0.305	0.802	-0.089	0.529
Ni	-0.162	0.732	-0.377	0.453
Pd	0.207	0.74	-0.31	0.481
Pt	0.127	0.778	-0.356	0.491
Rh	0.24	0.689	-0.324	0.408

C-O	CH3-O		CH2OH-O	
Metal	ΔU (eV)	Ea (eV)	ΔU (eV)	Ea (eV)
Ag	-1.667	0.756	-2.039	0.14
Au	-0.853	0.931	-1.091	0.451
Cu	-0.516	1.751	-0.808	0.827
Ir	0.361	2.052	0.23	1.995
Ni	1.021	1.45	0.962	1.296
Pd	0.301	1.878	0.291	1.125
Pt	-0.021	2.356	0.218	2.135
Rh	0.542	1.571	0.598	1.419

C-OH	CH3-OH		CH2OH-OH	
Metal	ΔU (eV)	Ea (eV)	ΔU (eV)	Ea (eV)
Ag	-0.857	1.37	-1.28	0.835
Au	-1.207	1.241	-1.511	0.705
Cu	-0.171	1.78	-0.685	1.089
Ir	-0.347	1.694	-0.528	1.108
Ni	0.276	2.037	0.128	1.645
Pd	-0.346	1.539	-0.464	1.2323
Pt	-0.584	1.267	-0.693	1.143
Rh	0.009	1.946	-0.034	1.598

SI2: Tabularised Helmholtz free energy changes and free energy barriers for the energy profiles found in the main text (fig. 2/4)

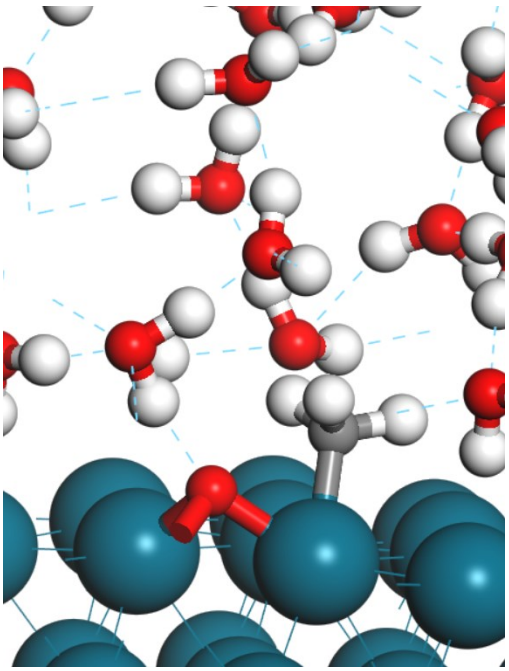
Gas	CH4		CH3OH	
Step	ΔF	Ea (eV)	ΔF	Ea (eV)
C-H	-1.15	0.37	-1.24	0.34
C-O	0.01	1.03	-0.15	0.69
C-OH	0.11	1.26	-0.04	1.04

Aq	CH4		CH3OH	
Step	ΔF	Ea (eV)	ΔF	Ea (eV)
C-H	-0.37	0.64	-0.43	0.54
C-O	0.54	1.35	0.00	0.99
C-OH	0.22	1.30	0.06	1.14

SI3: Total energy changes and total energy barriers for extra elementary steps considered for the Pd(111) surface

Elementary Step	ΔU (eV)	Ea (eV)
CH3O* + H* -> CH3OH	-0.46	0.59
CH3O* -> CH2O*+H*	-0.34	0.27

SI4a: Snapshot of the C-O coupling elementary step for methane in the aqueous phase. The R-R coordinate is at the 2.1Å window, close to the transition state distance.



SI4b: Local radial distribution function for surface oxygen to hydrogen for the simulation of SI4a. The first peak at 2 Å correlates to the coordinating water molecule, whilst the second peak correlates to the hydrogen of the methyl group.