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Supporting Information

Methanol dissociation on bimetallic surfaces: validity of general Brønsted-Evans-Polanyi relationship for O—H bond cleavage

José L. C. Fajín, [a,*] M. Natália D. S. Cordeiro[a] and José R. B. Gomes[b]

[a]*LAQV@REQUIMTE, Faculdade de Ciências, Universidade do Porto, P-4169-007 Porto, Portugal*

[b]*CICECO, Departamento de Química, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal*

*Corresponding Author: e-mail: jfajin@fc.up.pt. Fax: +351 220 402 659 (JLCF)

Table S1. Adsorption energies (E_{ads}, eV) for methanol on several bimetallic surfaces.

Surface	**Adsorption site**[a]	$E_{\mathrm{ads}}^{\mathrm{e}}$ [b]	$E_{\mathrm{ads}}^{\mathrm{o}}$ [b]	d [c]
Au@Cu(110)	t_M	-0.21	-0.19	2.24 (O)
Au@Pd(111)	undetermined	-0.04	-0.03	2.66 (H-(O))
Pd@Cu(110)	t_D	-0.23	-0.20	2.43 (O)
Pd@Cu(111)	undetermined	-0.03	0.00	2.76 (H-(O))
Rh@Cu(110)	t_D	-0.34	-0.31	2.31 (O)
Rh@Ir(110)	t_D	-0.52	-0.49	2.25 (O)
Rh@Ni(111)	undetermined	-0.05	-0.05	2.67 (H-(O))
Rh@Ni(110)	t_D	-0.37	-0.34	2.33 (O)
Ru@Au(110)	t_D	-0.63	-0.59	2.21 (O)
Ru@Cu(110)	t_D	-0.53	-0.49	2.25 (O)
Ru@Ni(111)	t_D	-0.22	-0.20	2.33 (O)
Ru@Ni(110)	t_D	-0.46	-0.43	2.30 (O)
Zn@Pd(111)	undetermined	-0.05	-0.04	2.69 (H-(O))
Zn@Pd(110)	t_D	-0.36	-0.34	2.22 (O)

[a]Labels for adsorption sites are provided in Fig. 1.

[b]Labels *e* and *o* stand for ZPV uncorrected and corrected adsorption energy values, respectively.

[c]Nearest-neighbor distance (Å) between methanol (H_{OH} atom in the case of the undermined adsorption site and O atom in the remaining cases) and an atom on the catalyst model surface.

Table S2. Co-adsorption energies ($E_{\mathrm{co-ads}}$, eV) for CH_3O+H pair on several bimetallic surfaces.

Surface	Adsorption site[a]	$E^{\mathrm{e}}_{\mathrm{co-ads}}$ [b]	$E^{\mathrm{o}}_{\mathrm{co-ads}}$ [b]	d [c]
Au@Cu(110)	S_D / S_M	0.25	0.13	1.94 (Cu)
Au@Pd(111)	f / h	0.61	0.48	2.16 (Pd)
Pd@Cu(110)	S_D / S_M	-0.07	-0.15	1.92 (Cu)
Pd@Cu(111)	f / h	0.41	0.31	2.03 (Cu)
Rh@Cu(110)	S_D / S_M	-0.39	-0.50	1.96 (Cu)
Rh@Ir(110)	S_D / S_M	-0.91	-1.02	2.02 (Ir)
Rh@Ni(111)	f / h	-0.15	-0.24	2.00 (Ni)
Rh@Ni(110)	S_D / S_M	-0.91	-1.02	1.90 (Ni)
Ru@Au(110)	t_D / S_M	-0.43	-0.55	1.88 (Ru)
Ru@Cu(110)	S_D / S_M	-0.83	-0.94	1.99 (Cu)
Ru@Ni(111)	f / h	-0.42	-0.50	2.02 (Ni)
Ru@Ni(110)	S_D / S_M	-1.00	-1.09	1.94 (Ni)
Zn@Pd(111)	g / f	0.01	-0.09	2.05 (Zn)
Zn@Pd(110)	S_D / S_M	-0.22	-0.33	1.98 (Zn)

[a]Labels for adsorption sites are provided in Fig. 1 and these are given here in the CH_3O / H order.

[b]In adsorption energies *e* and *o* stand for ZPV uncorrected and corrected values, respectively.

[c]Shorter distance (Å) between the methoxide and the surface; between parenthesis is given the surface atom interacting with the methoxide which interacts always through the O atom.

Table S3. Activation energy barriers (E_{act}, eV), imaginary frequencies (cm^{-1}), distances (d, Å) for the O—H bond cleaving in [CH_3OH^* + * → CH_3O^* + H*] reaction on several bimetallic surfaces, rate constants (k, s^{-1}) at 463 K, 503 K, 523 K and 573 K and, reaction energies (E_{react}).

Surface	υ [a]	$d_{O\cdots H}$ [b]	E_{act}^{e}	E_{act}^{o}	$E_{act}^{o,BEP}$ (Δ) [d]	$E_{act}^{o,BEP}$ (Δ) [e]	E_{react}^{e}	E_{react}^{o}	*k* (463 K)	*k* (503 K)	*k* (523 K)	*k* (573 K)
Au@Cu(110)	1008	1.54	1.01	0.96	0.85 (-0.11)	0.92 (-0.04)	0.46	0.48	2.71×10^{02}	1.97×10^{03}	4.76×10^{03}	3.31×10^{04}
Au@Pd(111)	485	1.77	1.44	1.25	1.00 (-0.25)	1.11 (-0.14)	0.65	0.54	7.01×10^{-01}	1.08×10^{01}	3.64×10^{01}	5.39×10^{02}
Pd@Cu(110)	1069	1.51	0.88	0.65	0.73 (0.08)	0.76 (0.11)	0.19	0.05	4.42×10^{04}	1.70×10^{05}	3.08×10^{05}	1.15×10^{06}
Pd@Cu(111)	572	1.72	1.34	1.16	0.93 (-0.23)	1.02 (-0.14)	0.44	0.34	5.25×10^{-01}	6.08×10^{00}	1.81×10^{01}	2.02×10^{02}
Rh@Cu(110)	1210	1.43	0.85	0.62	0.58 (-0.04)	0.56 (-0.06)	-0.05	-0.20	2.00×10^{05}	7.34×10^{05}	1.31×10^{06}	4.67×10^{06}
Rh@Ir(110)	997	1.39	0.23	0.03	0.35 (0.32)	0.27 (0.24)	-0.39	-0.53	5.22×10^{11}	5.73×10^{11}	5.99×10^{11}	6.63×10^{11}
Rh@Ni(111)	947	1.52	0.75	0.56	0.35 (-0.14)	0.27 (-0.22)	-0.10	-0.18	6.87×10^{05}	2.44×10^{06}	4.31×10^{06}	1.53×10^{07}
Rh@Ni(110)	972	1.55	0.70	0.49	0.69 (0.13)	0.71 (0.15)	-0.54	-0.68	6.41×10^{06}	1.74×10^{07}	2.70×10^{07}	7.17×10^{07}
Ru@Au(110)	338	1.63	0.75	0.57	0.56 (-0.01)	0.53 (-0.04)	0.20	0.04	9.01×10^{05}	2.89×10^{06}	4.84×10^{06}	1.51×10^{07}
Ru@Cu(110)	1298	1.38	0.78	0.55	0.39 (-0.16)	0.31 (-0.24)	-0.30	-0.45	4.87×10^{05}	1.44×10^{06}	2.32×10^{06}	6.63×10^{06}
Ru@Ni(111)	1076	1.46	0.60	0.39	0.58 (0.19)	0.56 (0.17)	-0.20	-0.30	2.44×10^{08}	5.87×10^{08}	8.69×10^{08}	2.08×10^{09}
Ru@Ni(110)	1249	1.35	0.59	0.36	0.32 (-0.04)	0.23 (-0.13)	-0.54	-0.67	6.08×10^{07}	1.24×10^{08}	1.71×10^{08}	3.44×10^{08}
Zn@Pd(111)	646	1.57	0.82	0.65	0.75 (0.10)	0.79 (0.14)	0.06	-0.03	4.14×10^{04}	1.62×10^{05}	2.97×10^{05}	1.14×10^{06}
Zn@Pd(110)	908	1.50	0.78	0.56	0.65 (0.09)	0.66 (0.10)	0.14	0.01	3.77×10^{05}	1.16×10^{06}	1.90×10^{06}	5.67×10^{06}

[a] Imaginary frequency in cm^{-1}.

[b] Length of the O—H breaking bond in the TS structure.

[c] In activation and reaction energies *e* and *o* stand for ZPV uncorrected and corrected values, respectively.

[d] Estimated activation energy barrier values using the general BEP relationship obtained in Ref. 28; values in parentheses are differences to the values obtained from the exhaustive location of the transition state structures with DFT.

[e]Estimated activation energy barrier values using the BEP relationship obtained in this work and which equation is displayed in Figure 3; values in parentheses are differences to the values obtained from the exhaustive location of the transition state structures with DFT.

Table S4. Co-adsorption energies ($E_{\mathrm{co-ads}}$) for CH_3O and H and estimated activation energy barriers ($E_{\mathrm{act}}^{\mathrm{o,\,BEP}}$) for the methanol O—H bond dissociation on bimetallic surfaces. Values in eV.

Surface	**Adsorption site**[a]	$E_{\mathrm{co-ads}}^{\mathrm{e}}$ [b]	$E_{\mathrm{co-ads}}^{\mathrm{o}}$ [b]	d [c]	$E_{\mathrm{act}}^{\mathrm{o,\,BEP}}$
Ag@Cu(110)	S_D / S_M	-0.04	-0.16	1.91 (Cu)	0.73
Ag@Cu(111)	f / h	0.70	0.59	2.05 (Cu)	1.05
Ag@Ni(111)	h / g	0.16	0.07	2.00 (Ni)	0.83
Ag@Ni(110)	L_M / C_M	-0.43	-0.53	1.98 (Ni)	0.56
Ir@Au(110)	S_D / S_M	-0.09	-0.21	1.96 (Ir)	0.70
Ni@Au(110)	S_D / S_M	0.15	0.02	1.86 (Ni)	0.80
Ni@Cu(111)	f / h	-0.24	-0.33	1.98 (Ni)	0.65
Ni@Pd(110)	S_D / S_M	-0.52	-0.63	1.87 (Ni)	0.52
Pt@Cu(110)	S_D / S_M	-0.01	-0.11	1.98 (Cu)	0.74
Pt@Cu(111)	f / h	0.60	0.48	2.06 (Cu)	1.00
Pt@Ni(111)	f / h	0.82	0.72	1.98 (Ni)	1.11
Rh@Cu(111)	f / h	-0.15	-0.25	2.08 (Cu)	0.69
Rh@Pd(111)	f / h	-0.09	-0.20	2.05 (Rh)	0.71
Ru@Cu(111)	f / h	-0.58	-0.68	2.05 (Ru)	0.50
Ru@Pd(111)	f / h	-0.41	-0.52	2.01 (Ru)	0.57

[a]Labels for adsorption sites are provided in Fig. 1 and these are given here in the CH_3O / H order.

[b]In adsorption energies *e* and *o* stand for ZPV uncorrected and corrected values, respectively.

[c]Shorter distance (Å) between the methoxide and the surface; between parenthesis is given the surface atom interacting with the methoxide which interacts always through the O atom.