Hydrogen Complexes on Single Atom Alloys: Classical Chemisorption versus Coordination Chemistry

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Supporting Information

Section S1: Structural information

Table S1: Cell parameter *a* and space group of the optimized bulk metals.

M	*a* /Å	Space group
Mo	3.136	229
Rh	3.793	225
Ag	4.067	225
Pd	3.888	225
Nb	3.261	229
Ni	3.474	225
Au	4.103	225
Ru	2.696	194

Table S2: Cell parameters *a, b* and *γ* of the adopted metal slabs.

M	*a* /Å	*b* /Å	γ /°
Mo (110)	9.407	8.869	90
Rh (111)	5.364	5.364	120
Ag (111)	5.752	5.752	120
Pd (111)	5.499	5.499	120
Nb (110)	9.780	9.220	90
Ni (111)	4.913	4.913	120
Au (111)	5.802	5.802	120
Ru (0001)	5.393	5.393	120

Section S2: Working equations

The adsorption of H adatom and complexes (ΔE and ΔG, respectively) were calculated according to the following equations, where E_{tot} is the energy of the catalyst with adsorbed H and H_2, E_{H2} and E_{cat} are the energies of the isolated hydrogen molecule and catalyst, respectively. The Gibbs free energy were estimated by including the thermodynamics correction according to the seminal approach of Norskov and co-workers. The entropic contribution of solid-state species was

neglected, the entropy of gas phase H_2 was taken from international tables; at 298 K, $T\Delta S_H$, is equal to 0.40 eV. The zero-point energy correction term, ΔE_{ZPE}, is often small (less than 0.1 eV. We adopt the value 0.04 eV, following Ref. [1], which is a representative case of atomic H adsorbed on several metal surfaces.[1–3]

$\Delta E_H = E_{tot} - E_{H2} * 0.5 - E_{cat}$
$\Delta E_{H2} = E_{tot} - E_{H2} - E_{cat}$

The exchange current, $Log(i_0)$ for hydrogen evolution reaction over the different metal surfaces as a function of the calculated hydrogen chemisorption free energy (ΔG_{H^*}) was obtained according to Ref. [1]:

for $\Delta G_{H^*}<0$: $i_0 = -ek_0 \frac{1}{1+exp\left(-\Delta G_H / k_B T\right)}$

for $\Delta G_{H^*}>0$: $i_0 = -ek_0 \frac{1}{1+exp\left(-\Delta G_H / k_B T\right)} exp\left(-\Delta G_H / k_B T\right)$

Section S3: additional information for H and H_2 adsorption on SAAs

Table S3: Unpaired electrons and atomic magnetizations of the dopant metals atom in the SAA system.

System	Magnetization /μ_B	Unpaired electrons
Ti@Ag(111)	1.10	1
Fe@Ag(111)	2.91	3
Co@Ag(111)	1.51	2
W@Ag(111)	2.22	2
Ir@Ag(111)	0.00	0
Pt@Ag(111)	0.00	0
Ti@Au(111)	0.00	0
Fe@Au(111)	3.00	3
Co@Au(111)	1.69	2
W@Au(111)	1.62	2
Ir@Au(111)	0.00	0
Pt@Au(111)	0.00	0
Ti@Rh(111)	0.00	0

Fe@Rh(111)	2.79	3
Co@Rh(111)	1.32	1
W@Rh(111)	0.00	0
Ir@Rh(111)	0.00	0
Pt@Rh(111)	0.00	0
Ti@Pd(111)	0.12	0
Fe@Pd(111)	0.29	0
Co@Pd(111)	2.18	2
W@Pd(111)	0.03	0
Ir@Pd(111)	1.06	1
Pt@Pd(111)	0.30	0
Ti@Ni(111)	0.17	0
Fe@Ni(111)	2.87	3
Co@Ni(111)	1.74	2
W@Ni(111)	0.01	0
Ir@Ni(111)	0.59	1
Pt@Ni(111)	0.11	0
Ti@Ru(0001)	0.01	0
Fe@Ru(0001)	2.46	2
Co@Ru(0001)	0.16	0
W@Ru(0001)	0.03	0
Ir@Ru(0001)	0.03	0
Pt@Ru(0001)	0.02	0
Ti@Mo(110)	0.00	0
Fe@Mo(110)	2.41	2

Co@Mo(110)	1.44	1
W@Mo(110)	0.00	0
Ir@Mo(110)	0.00	0
Pt@Mo(110)	0.00	0
Ti@Nb(110)	0.23	0
Fe@Nb(110)	0.00	0
Co@Nb(110)	0.00	0
W@Nb(110)	0.00	0
Ir@Nb(110)	0.00	0
Pt@Nb(110)	0.00	0

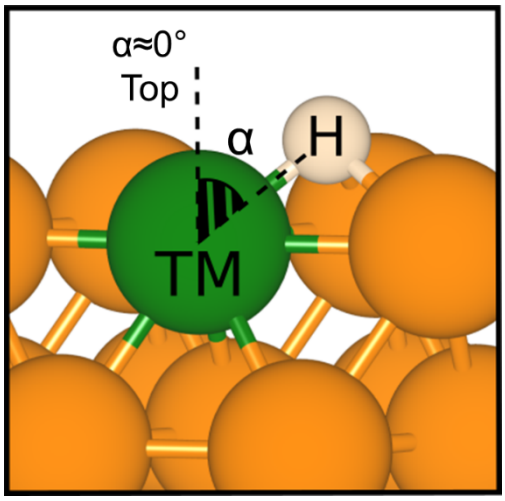

Figure S1: Definition of the angle α between the H atom and the normal to the TM atom on the surface.

Table S4: Free energy, distances, and isomer type for H* and H-H* species interacting with the guest metal on Ag and Au metal slab using different levels of theory. In bold are the results employing the PBE+*U** approach. We label with A the guest TM atom, and with B the hosting supporting metal.

	H					**H_2**			
	Site[(a)]	ΔG /eV	d_{A-H} /Å	d_{B-H} /Å	α /°	Structure	ΔG /eV	d_{A-H} /Å	d_{H-H} /Å

Ag(111)	H	0.36	//	1.90	62.3	2H*	0.64	1.88	2.88
Ti@Ag(111)	**H**	**0.05**	**1.93**	**1.96**	**57.0**	**H*H***	**-0.05**	**1.92**	**2.64**
Ti@Ag(111)	H	-0.06	1.85	2.03	52.3	H*H*	-0.26	1.87	2.57
Fe@Ag(111)	**H**	**0.02**	**1.74**	**1.97**	**57.4**	**H*H***	**0.09**	**1.75**	**2.57**
Fe@Ag(111)	H	-0.06	1.70	1.99	56.8	H*H*	-0.17	1.70	2.42
Co@Ag(111)	**H**	**0.76**	**1.69**	**1.94 1.96**	**58.6**	**H*H***	**0.14**	**1.73**	**2.56**
Co@Ag(111)	H	-0.03	1.58	2.10	47.1	H_2*	-0.14	1.51	1.04
W@Ag(111)	**H**	**-0.15**	**1.79**	**2.21**	**44.6**	**H*H***	**-0.43**	**1.79**	**2.11**
W@Ag(111)	H	-0.33	1.77	2.24	43.4	H*H*	-0.83	1.75	2.00
Ir@Ag(111)	**T**	**-0.59**	**1.57**	**//**	**0.0**	**H*H***	**-0.97**	**1.60**	**1.90**
Ir@Ag(111)	T	-0.51	1.59	//	0.0	H*H*	-0.89	1.62	1.95
Pt@Ag(111)	**H**	**-0.01**	**1.62**	**2.23**	**44.6**	**H*H***	**0.04**	**1.65**	**2.34**
Pt@Ag(111)	H	-0.03	1.64	2.22	44.7	H*H*	-0.02	1.67	2.35
Au(111)	H	0.471	//	1.88 1.86 1.96	64.1	2H*	0.859	1.87 1.91	2.90
Ti@Au(111)	**H**	**0.15**	**2.00**	**1.91**	**57.2**	H_2*	**0.18**	**2.06**	**0.78**
Ti@Au(111)	H	0.08	1.88	2.01	55.2	H_2*	0.09	2.07	0.78
Fe@Au(111)	**H**	**0.24**	**1.94**	**1.87**	**59.9**	**2H***	**0.42**	**1.91**	**2.76**
Fe@Au(111)	H	0.30	1.77	1.96	56.7	2H*	0.28	1.90	2.76
Co@Au(111)	**H**	**0.18**	**1.90**	**1.88 1.86**	**57.8**	**2H***	**0.34**	**1.86**	**2.75**
Co@Au(111)	H	0.07	1.67	1.99	57.4	H_2*	0.01	1.62	0.87
W@Au(111)	**T**	**-0.12**	**1.72**	**//**	**0.0**	**H*H***	**-0.33**	**1.74**	**1.87**
W@Au(111)	T	-0.41	1.72	//	0.0	H*H*	-0.70	1.73	1.85
Ir@Au(111)	**T**	**-0.57**	**1.57**	**//**	**0.0**	**H*H***	**-0.85**	**1.58**	**1.70**

Ir@Au(111)	T	-0.64	1.58	//	0.0	H*H*	-0.90	1.60	1.75
Pt@Au(111)	**T**	**-0.10**	**1.54**	//	**0.0**	**H*H***	**0.28**	**1.66**	**2.29**
Pt@Au(111)	T	-0.11	1.56	//	0.0	H*H*	0.19	1.69	2.32

*U parameter employed on the guest transition metal atom:

TM	U^{4-6}
Ti	2.58
Fe	3.29
Co	3.42
W	2.08
Ir	2.74
Pt	2.95

Table S5: Adsorption energy for H* and H-H* species interacting with the guest metal on Au and Ag metal slabs.

	H	**H_2**
	ΔE /eV	ΔE /eV
Ag(111)	0.12	0.16
Ti@Ag(111)	-0.30	-0.75
Fe@Ag(111)	-0.31	-0.65
Co@Ag(111)	-0.28	-0.62
W@Ag(111)	-0.57	-1.32
Ir@Ag(111)	-0.76	-1.37
Pt@Ag(111)	-0.28	-0.50
Au(111)	0.23	0.38
Ti@Au(111)	-0.17	-0.39
Fe@Au(111)	0.05	-0.21
Co@Au(111)	-0.18	-0.47
W@Au(111)	-0.66	-1.18
Ir@Au(111)	-0.88	-1.38
Pt@Au(111)	-0.36	-0.22

Table S6: Adsorption energy for H* and H-H* species interacting with the guest metal on Rh, Pd, Ni, and Ru metal slabs.

	H	**H_2**
	ΔE /eV	ΔE /eV
Rh(111)	-0.53	-1.18
Ti@Rh(111)	-0.79	-1.55
Fe@Rh(111)	-0.60	-1.24
Co@Rh(111)	-0.60	-1.26
W@Rh(111)	-0.63	-0.64
Ir@Rh(111)	-0.64	-1.22
Pt@Rh(111)	-0.47	-1.02
Pd(111)	-0.55	-1.12
Ti@Pd(111)	-0.61	-1.12
Fe@Pd(111)	-0.68	-2.47
Co@Pd(111)	-0.51	-1.01
W@Pd(111)	-0.53	-0.95
Ir@Pd(111)	-0.74	-1.48
Pt@Pd(111)	-0.61	-1.10
Ni(111)	-0.63	-1.30
Ti@Ni(111)	-0.82	-1.59
Fe@Ni(111)	-0.56	-1.15
Co@Ni(111)	-0.60	-1.27
W@Ni(111)	-0.61	-1.12
Ir@Ni(111)	-0.55	-1.12
Pt@Ni(111)	-0.44	-0.87

Ru(0001)	-0.58	-1.11
Ti@Ru(0001)	-0.77	-1.50
Fe@Ru(0001)	-0.55	-1.17
Co@Ru(0001)	-0.62	-1.26
W@Ru(0001)	-0.61	-1.20
Ir@Ru(0001)	-0.45	-0.98
Pt@Ru(0001)	-0.29	-1.20

Table S7: Adsorption energy for H* and H-H* species interacting with the guest metal on Mo and Nb metal slabs.

	H	**H_2**
	ΔE /eV	ΔE /eV
Mo(110)	-0.83	-1.63
Ti@Mo(110)	-1.00	-0.13
Fe@Mo(110)	-0.61	-1.47
Co@Mo(110)	-0.86	-1.50
W@Mo(110)	-0.89	-0.02
Ir@Mo(110)	-0.66	-1.20
Pt@Mo(110)	-1.01	-1.01
Nb(110)	-1.43	-2.47
Ti@Nb(110)	-1.26	-2.40
Fe@Nb(110)	-0.94	-1.84
Co@Nb(110)	-0.89	-1.68
W@Nb(110)	-1.11	-2.13
Ir@Nb(110)	-0.80	-1.39

Pt@Nb(110)	-0.72	-2.22

Table S8: Calculated desorption temperatures of hydrogen adsorbates on Au and Ag-based SAAs assuming a first-order Redhead model.

		ΔE /eV	T / K
Au metal		0.379	/
Au	Ti	-0.388	145
	Fe	-0.206	75
	Co	-0.468	170
	W	-1.180	425
	Ir	-1.378	245
	Pt	-0.223	85 145
Ag metal		0.159	/
Ag	Ti	-0.745	275
	Fe	-0.653	240
	Co	-0.621	230
	W	-1.315	470
	Ir	-1.369	490
	Pt	-0.499	185

Table S9: Calculated desorption temperatures of hydrogen adsorbates on Rh, Pd, Ni, and Ru-based SAAs assuming a first-order Redhead model.

		ΔE /eV	T / K
Rh metal		-1.179	425
Rh	Ti	-1.550	550
	Fe	-1.238	440
	Co	-1.260	450
	W	-0.644	235
	Ir	-1.216	435
	Pt	-1.021	370
Pd metal		-1.116	400

Pd	Ti	-1.118	400
	Fe	-2.466	865
	Co	-1.011	365
	W	-0.945	345
	Ir	-1.482	530
	Pt	-1.104	395
Ni metal		-1.302	465
Ni	Ti	-1.588	565
	Fe	-1.146	410
	Co	-1.270	455
	W	-1.124	400
	Ir	-1.120	400
	Pt	-0.870	315
Ru metal		-0.58	212
Ru	Ti	-0.77	278
	Fe	-0.55	202
	Co	-0.62	225
	W	-0.61	223
	Ir	-0.45	167
	Pt	-0.29	110

Table S10: Calculated desorption temperatures of hydrogen adsorbates on Mo and Nb-based SAAs assuming a first-order Redhead model.

		ΔE /eV	T / K
Mo metal		-1.63	580
Mo	Ti	-0.13	45
	Fe	-1.47	525
	Co	-1.50	535
	W	-0.02	<20
	Ir	-1.20	430
	Pt	-1.01	365
Nb metal		-2.47	870
Nb	Ti	-2.40	840
	Fe	-1.84	650

	Co	-1.68	600
	W	-2.13	750
	Ir	-1.39	500
	Pt	-2.22	785

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