Supplementary Information (SI) for Nanoscale.

First principle investigation of hydrogen passivation for selective atomic layer deposition of Pt, Cu, and Au metals

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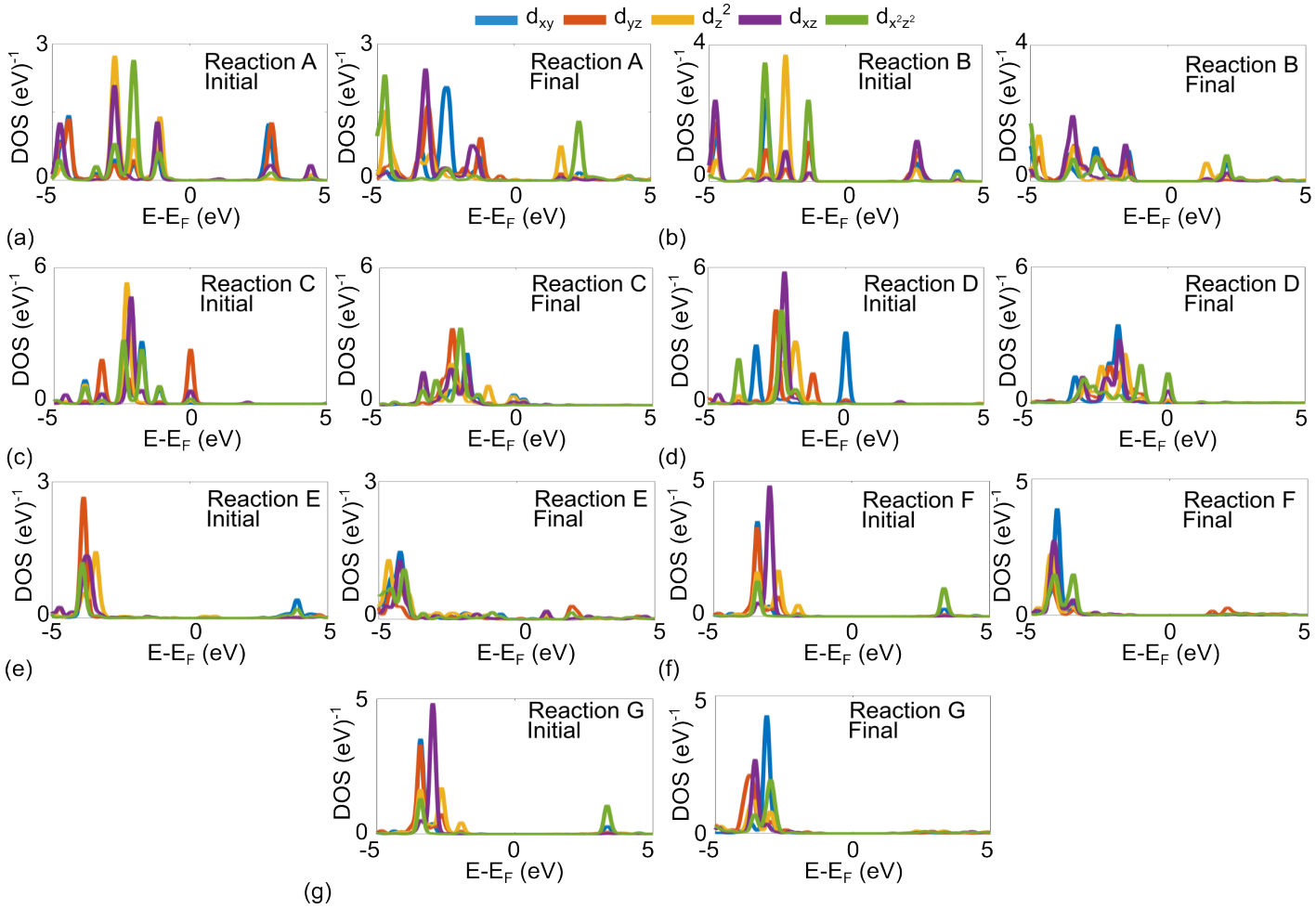

Figure 1: Projected density of states (PDOS) onto the d orbitals of the metal atom in the precursor for Reactions A–G, shown in panels (a)–(g), respectively. In each panel, the left side shows the PDOS before and after interaction with the Si(100) or H–Si(100) substrate. Comparisons highlight changes in d-orbital features upon adsorption, providing insight into the degree of hybridization and the nature of the precursor–surface interaction.

Table 1: Table reporting the values for Entropy, enthalpy and Gibbs Free energy, for all the temperatures analyzed for all Metals (Pt, Cu, Au).

		T*S ORCA [Kcal/mol]		**H ORCA [Kcal/mol]**		$\Delta G = \Delta H - \Delta TS$			
		S Final Step	**S Initial Step**	**H Final Step**	**H Initial Step**	ΔTS	ΔH	ΔG	
Me_3AuPMe_3 **273.15K**	**A**	79.2548	79.6121	-5751457.3753	-5751402.7568	-0.3573	-54.6184	-54.2612	Spontaneous at Low T
	B	82.9830	80.8537	-5754505.0068	-5754470.0232	2.1293	-34.9837	-37.1130	Spontaneous at all T
Me_3AuPMe_3 **298.15K**	**A**	92.0604	92.6192	-5751451.5633	-5751396.9630	-0.5588	-54.6002	-54.0415	Spontaneous at Low T
	B	96.5712	93.0116	-5754498.7154	-5754464.4226	3.5596	-34.2928	-37.8523	Spontaneous at all T
Me_3AuPMe_3 **373.15K**	**A**	134.8598	135.5590	-5751432.4826	-5751377.6734	-0.6992	-54.8092	-54.1100	Spontaneous at Low T
	B	142.0898	139.2755	-5754477.9863	-5754443.1551	2.8143	-34.8312	-37.6454	Spontaneous at all T
$Cu(acac)_2$ **273.15K**	**A**	84.6556	83.7551	-6917712.8076	-6917673.1583	0.9004	-39.6493	-40.5498	Spontaneous at all T
	B	87.7405	84.9564	-6920747.8167	-6920748.3795	2.7841	0.5628	-2.2213	Spontaneous at all THigh T
$Cu(acac)_2$ **298.15K**	**C**	98.2586	97.2185	-6917706.6380	-6917667.0735	1.0401	-39.5645	-40.6046	Spontaneous at all T
	D	102.0247	98.9597	-6920741.2368	-6920741.8644	3.0650	0.6275	-2.4375	Spontaneous at High T
$Cu(acac)_2$ **373.15K**	**E**	143.5451	142.0592	-6917686.4562	-6917647.1316	1.4858	-39.3246	-40.8105	Spontaneous at all T
	F	149.8548	145.9284	-6920719.5186	-6920720.3624	3.9264	0.8438	-3.0826	Spontaneous at High T
Me_3AuPMe_3 **273.15K**	**E**	76.4219	67.9210	-5904842.3398	-5904748.7964	8.5008	-93.5434	-102.0443	Spontaneous at all T
	F	84.9613	82.1515	-5907973.6293	-5907944.5383	2.8099	-29.0910	-31.9008	Spontaneous at all T
	G	83.2554	82.1518	-5907928.9793	-5907944.5389	1.1036	15.5596	14.4559	Spontaneous at High T
Me_3AuPMe_3 **298.15K**	**E**	88.8272	79.3346	-5904836.7043	-5904743.5392	9.4926	-93.1651	-102.6577	Spontaneous at all T
	F	98.8271	95.7714	-5907967.2512	-5907938.2038	3.0557	-29.0474	-32.1031	Spontaneous at all T
	G	97.0407	95.7793	-5907922.6133	-5907938.2395	1.2614	15.6262	14.3649	Spontaneous at High T
Me_3AuPMe_3 **373.15K**	**E**	130.3238	117.6907	-5904818.2347	-5904726.1651	12.6331	-92.0697	-104.7028	Spontaneous at all T
	F	145.1636	141.4363	-5907946.3200	-5907917.3424	3.7273	-28.9776	-32.7049	Spontaneous at all T
	G	143.0824	141.4366	-5907901.6007	-5907917.3429	1.6458	15.7423	14.0965	Spontaneous at High T

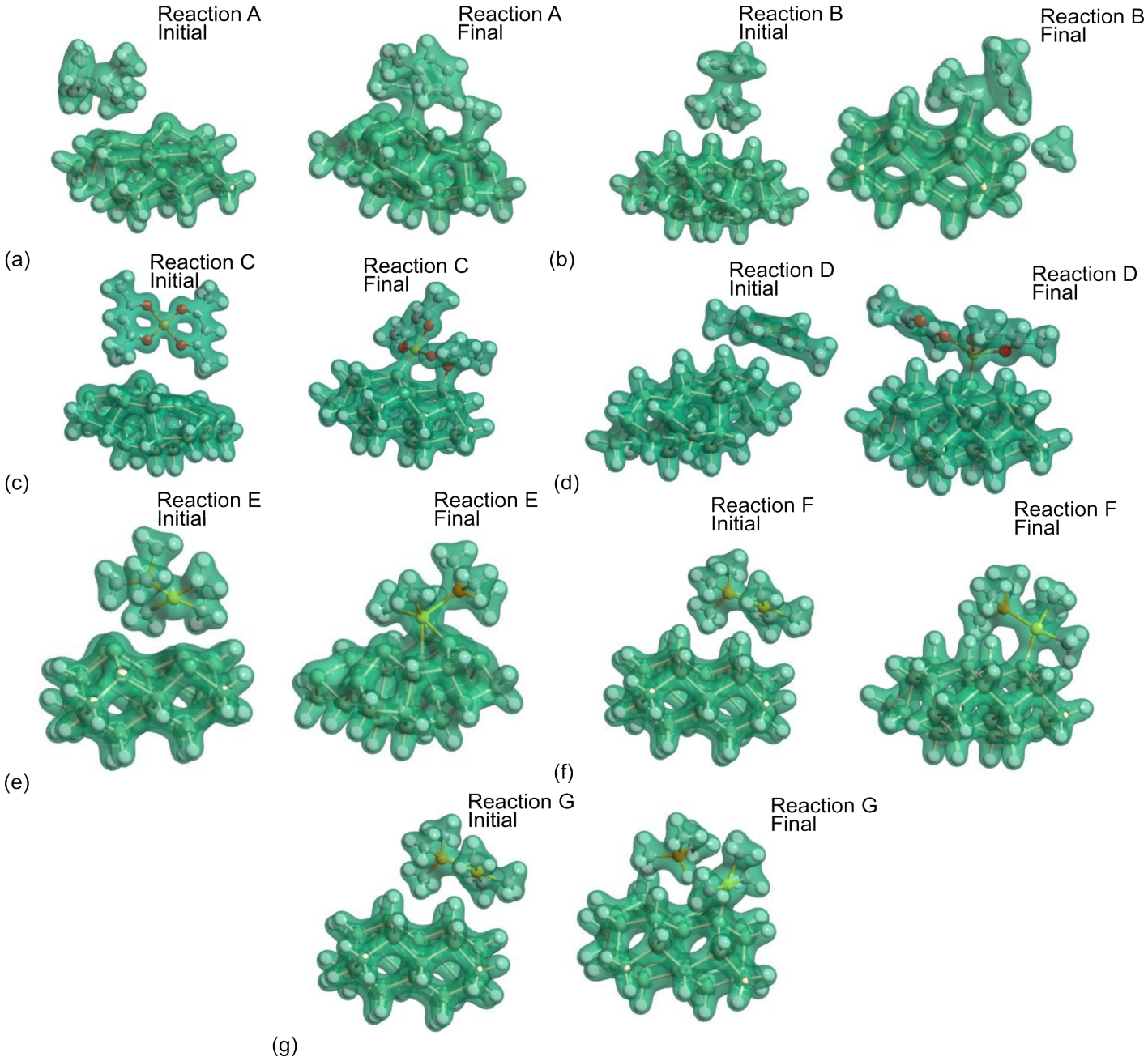

Figure 2: Electron density plots for Reactions A–G, shown in panels (a)–(g), respectively. Each panel illustrates the charge redistribution upon adsorption of the precursor on the Si(100) or H–Si(100) surface. In all cases, an isovalue equal to 0.3 $Å^{-3}$ is considered.

Reaction		Initial state [e]	Final state [e]
A	Precursor	0.0120428303708	0.105269448315
	Substrate	-0.0120428303706	-0.105269448238
B	Precursor	0.00544528489243	0.0131105298932
	Substrate	-0.00544528489161	-0.0131105298925
C	Precursor	0.040967419284	0.117565432675
	Substrate	-0.0409674192548	-0.117565432772
D	Precursor	0.0481875713274	0.103194763725
	Substrate	-0.0598857011368	-0.111322277312
E	Precursor	-0.0546376581764	0.146259559312
	Substrate	0.0546376581763	-0.146259559272
F	Precursor	0.0291139828143	0.116546227398
	Substrate	-0.0291139828145	-0.116546227398
G	Precursor	0.0291139828143	0.193717811962
	Substrate	-0.0291139828145	-0.193717811963

Table 2: Electronic charge (in units of e) transferred during the initial and final states for each reaction, distinguishing between precursor and substrate contributions.