Supporting Information

A Mechanistic Insight into Rhodium–Doped Gold Clusters as a Better Hydrogenation Catalyst

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Content Index

1. Thermodynamic Data (in a.u) of Ethylene Hydrogenation on Au_8 Cluster

[DFT:B3LYP-D3(BJ)/def2-TZVP (Rh,C,H)+LANL2DZ(f) (Au)]

Gas Phase

	Cluster	2	3	4	5*	6	7	8*	9	10*	11	12
E	-1084.038198	-1162.640993	-1163.813651	-1163.808307	-1163.786859	-1163.791957	-1163.81996	-1163.763914	-1163.826904	-1163.773777	-1163.835015	-1163.841846
U	-1084.021325	-1162.620005	-1163.789107	-1163.784335	-1163.765246	-1163.770182	-1163.798807	-1163.742899	-1163.80562	-1163.752613	-1163.812533	-1163.81944
H	-1084.020381	-1162.619061	-1163.788163	-1163.783391	-1163.764302	-1163.769238	-1163.797863	-1163.741955	-1163.804676	-1163.751669	-1163.811589	-1163.818496
G	-1084.10141	-1162.710189	-1163.888144	-1163.878653	-1163.852791	-1163.858043	-1163.885268	-1163.830851	-1163.893152	-1163.839693	-1163.905372	-1163.913711

Solvent Phase

(Solvent Model: SMD, Solvent: Ethanol)

	Cluster	2	3	4	5*	6	7	8*	9	10*	11	12
E	-1084.034765	-1162.638403	-1163.810352	-1163.804497	-1163.78343	-1163.788875	-1163.816396	-1163.760672	-1163.823611	-1163.771514	-1163.83163	-1163.838665
U	-1084.017904	-1162.61746	-1163.785955	-1163.780565	-1163.761809	-1163.767095	-1163.795256	-1163.739673	-1163.802362	-1163.750348	-1163.809238	-1163.816331
H	-1084.01696	-1162.616516	-1163.785011	-1163.779621	-1163.760865	-1163.766151	-1163.794311	-1163.738728	-1163.801418	-1163.749404	-1163.808294	-1163.815387
G	-1084.097244	-1162.707064	-1163.88346	-1163.874771	-1163.849418	-1163.854989	-1163.881637	-1163.827483	-1163.889684	-1163.837451	-1163.901584	-1163.909762

2. Thermodynamic Data (in a.u) of Ethylene Hydrogenation on Au_{20} Cluster

[DFT:B3LYP-D3(BJ)/def2-TZVP (Rh,C,H)+LANL2DZ(f) (Au)]

Gas Phase

	Cluster	2	3	4*	5	6*	7	8*	9	10*	11
E	-2710.412212	-2789.005905	-2790.177516	-2790.126909	-2790.134462	-2790.114689	-2790.161611	-2790.141146	-2790.183183	-2790.132508	-2790.220736
U	-2710.367206	-2788.957275	-2790.12445	-2790.076621	-2790.083698	-2790.065195	-2790.111855	-2790.091561	-2790.133806	-2790.082529	-2790.170072
H	-2710.366261	-2788.95633	-2790.123506	-2790.075677	-2790.082754	-2790.06425	-2790.11091	-2790.090617	-2790.132862	-2790.081585	-2790.169127
G	-2710.518828	-2789.118732	-2790.298753	-2790.243833	-2790.251603	-2790.22899	-2790.276847	-2790.256563	-2790.296278	-2790.247142	-2790.338159

Solvent Phase

(Solvent Model: SMD, Solvent: Ethanol)

	Cluster	2	3	4*	5	6*	7	8*	9	10*	11
E	-2710.405614	-2789.00012	-2790.171101	-2790.121304	-2790.12851	-2790.108178	-2790.155366	-2790.135091	-2790.177056	-2790.126842	-2790.214093
U	-2710.360624	-2788.951536	-2790.118187	-2790.071087	-2790.077835	-2790.058715	-2790.105634	-2790.085524	-2790.127735	-2790.076906	-2790.163549
H	-2710.35968	-2788.950592	-2790.117243	-2790.070143	-2790.076891	-2790.057771	-2790.10469	-2790.08458	-2790.126791	-2790.075962	-2790.162605
G	-2710.512138	-2789.112731	-2790.290629	-2790.237578	-2790.245224	-2790.222381	-2790.270597	-2790.250535	-2790.289717	-2790.241342	-2790.330494

3. Thermodynamic Data (in a.u) of Ethylene Hydrogenation on Au_8Rh Cluster

[DFT:B3LYP-D3(BJ)/def2-TZVP (Rh,C,H)+LANL2DZ(f) (Au)]

(G Pathway)

Gas Phase

	Cluster	2G	3G	4G*	5G	6G	7G*	8G	9G*	10G	11G*	12	13*	14
E	-1194.683689	-1273.301072	-1274.471804	-1274.445948	-1274.446747	-1274.471305	-1274.45074	-1274.48279	-1274.478354	-1274.481228	-1274.463832	-1274.469474	-1274.462404	-1274.492595
U	-1194.664701	-1273.278918	-1274.44658	-1274.422703	-1274.423454	-1274.448294	-1274.427894	-1274.459742	-1274.455572	-1274.458367	-1274.441019	-1274.446255	-1274.439301	-1274.468351
H	-1194.663756	-1273.277973	-1274.445636	-1274.421759	-1274.42251	-1274.44735	-1274.42695	-1274.458798	-1274.454628	-1274.457423	-1274.440075	-1274.44531	-1274.438357	-1274.467407
G	-1194.747202	-1273.368304	-1274.542649	-1274.513452	-1274.514079	-1274.539921	-1274.518401	-1274.550273	-1274.545389	-1274.548293	-1274.532714	-1274.537827	-1274.530984	-1274.564003

Solvent Phase

(Solvent Model: SMD, Solvent: Ethanol)

	Cluster	2G	3G	4G*	5G	6G	7G*	8G	9G*	10G	11G*	12	13*	14
E	-1194.679757	-1273.296771	-1274.46719	-1274.44159	-1274.442435	-1274.466776	-1274.446719	-1274.478559	-1274.474552	-1274.477694	-1274.460446	-1274.465987	-1274.458927	-1274.488775
U	-1194.660774	-1273.274631	-1274.442187	-1274.418361	-1274.419164	-1274.443784	-1274.423897	-1274.455525	-1274.451783	-1274.454848	-1274.437656	-1274.442829	-1274.435872	-1274.46462
H	-1194.659829	-1273.273687	-1274.441242	-1274.417416	-1274.41822	-1274.44284	-1274.422952	-1274.454581	-1274.450838	-1274.453903	-1274.436712	-1274.441885	-1274.434928	-1274.463676
G	-1194.743264	-1273.36417	-1274.537377	-1274.509052	-1274.509697	-1274.535257	-1274.514366	-1274.546009	-1274.541593	-1274.544741	-1274.52904	-1274.533797	-1274.52748	-1274.559654

(R Pathway)

Gas Phase

	Cluster	2R	3R	4R*	5R	6R*	12	13*	14
E	-1194.683689	-1273.295162	-1274.467784	-1274.466187	-1274.47006	-1274.461539	-1274.469474	-1274.462404	-1274.492595
U	-1194.664701	-1273.27283	-1274.444204	-1274.443209	-1274.446967	-1274.438699	-1274.446255	-1274.439301	-1274.468351
H	-1194.663756	-1273.271885	-1274.44326	-1274.442265	-1274.446023	-1274.437755	-1274.44531	-1274.438357	-1274.467407
G	-1194.747202	-1273.362099	-1274.535184	-1274.533791	-1274.537945	-1274.529893	-1274.537827	-1274.530984	-1274.564003

Solvent Phase

(Solvent Model: SMD, Solvent: Ethanol)

	Cluster	2R	3R	4R*	5R	6R*	12	13*	14
E	-1194.679757	-1273.291331	-1274.463994	-1274.462117	-1274.465925	-1274.457903	-1274.465987	-1274.458927	-1274.488775
U	-1194.660774	-1273.269023	-1274.440463	-1274.439145	-1274.442856	-1274.435043	-1274.442829	-1274.435872	-1274.46462
H	-1194.659829	-1273.268079	-1274.439519	-1274.438201	-1274.441912	-1274.434099	-1274.441885	-1274.434928	-1274.463676
G	-1194.743264	-1273.358202	-1274.531287	-1274.529728	-1274.533721	-1274.526554	-1274.533797	-1274.52748	-1274.559654

4. Thermodynamic Data (in a.u) of Ethylene Hydrogenation on $Au_{20}Rh$ Cluster

[DFT:B3LYP-D3(BJ)/def2-TZVP (Rh,C,H)+LANL2DZ(f) (Au)]

(G Pathway)

Gas Phase

	Cluster	2G	3G	4G*	5G	6G*	7G	8G*	9G	10G*	11	12	13
E	-2821.052811	-2899.66704	-2900.836657	-2900.792951	-2900.828537	-2900.815781	-2900.830862	-2900.824796	-2900.830514	-2900.808835	-2900.839686	-2900.830053	-2900.865448
U	-2821.005633	-2899.616501	-2900.782749	-2900.741459	-2900.776874	-2900.764381	-2900.779531	-2900.773756	-2900.779347	-2900.757232	-2900.788275	-2900.7787	-2900.813123
H	-2821.004689	-2899.615557	-2900.781805	-2900.740514	-2900.77593	-2900.763437	-2900.778587	-2900.772812	-2900.778402	-2900.756288	-2900.787331	-2900.777756	-2900.812179
G	-2821.164759	-2899.782178	-2900.956427	-2900.90846	-2900.944435	-2900.932069	-2900.946323	-2900.940264	-2900.945854	-2900.92616	-2900.955261	-2900.946826	-2900.984819

Solvent Phase

(Solvent Model: SMD, Solvent: Ethanol)

	Cluster	2G	3G	4G*	5G	6G*	7G	8G*	9G	10G*	11	12	13
E	-2821.045939	-2899.660324	-2900.829131	-2900.786077	-2900.82168	-2900.80885	-2900.823976	-2900.818369	-2900.824322	-2900.802706	-2900.833385	-2900.823928	-2900.858875
U	-2820.998774	-2899.60981	-2900.775366	-2900.734621	-2900.77004	-2900.757509	-2900.772675	-2900.767353	-2900.773192	-2900.75115	-2900.781995	-2900.772635	-2900.806601
H	-2820.99783	-2899.608866	-2900.774422	-2900.733677	-2900.769096	-2900.756565	-2900.771731	-2900.766408	-2900.772248	-2900.750206	-2900.781051	-2900.771691	-2900.805657
G	-2821.157815	-2899.775376	-2900.948422	-2900.901472	-2900.937517	-2900.924872	-2900.939341	-2900.933769	-2900.939562	-2900.919821	-2900.948941	-2900.940383	-2900.978158

(R Pathway)

Gas Phase

	Cluster	2R	3R	4R*	5R	6R*	11	12	13
E	-2821.052811	-2899.666109	-2900.844099	-2900.839932	-2900.84091	-2900.830235	-2900.839686	-2900.830053	-2900.865448
U	-2821.005633	-2899.6156	-2900.792603	-2900.788684	-2900.789535	-2900.779245	-2900.788275	-2900.7787	-2900.813123
H	-2821.004689	-2899.614656	-2900.791659	-2900.78774	-2900.788591	-2900.778301	-2900.787331	-2900.777756	-2900.812179
G	-2821.164759	-2899.78085	-2900.958828	-2900.954886	-2900.956227	-2900.945331	-2900.955261	-2900.946826	-2900.984819

Solvent Phase

(Solvent Model: SMD, Solvent: Ethanol)

	Cluster	2R	3R	4R*	5R	6R*	11	12	13
E	-2821.045939	-2899.659076	-2900.836997	-2900.832794	-2900.833932	-2900.823958	-2900.833385	-2900.823928	-2900.858875
U	-2820.998774	-2899.608585	-2900.785537	-2900.781577	-2900.78258	-2900.772983	-2900.781995	-2900.772635	-2900.806601
H	-2820.99783	-2899.607641	-2900.784593	-2900.780633	-2900.781635	-2900.772039	-2900.781051	-2900.771691	-2900.805657
G	-2821.157815	-2899.773852	-2900.951633	-2900.947639	-2900.949202	-2900.939012	-2900.948941	-2900.940383	-2900.978158

5. Thermodynamic Data (in a.u) of Ethylene and H_2

Gas Phase

	Ethylene	H_2
E	-78.576752	-1.169725
U	-78.573713	-1.167365
H	-78.572769	-1.166421
G	-78.597615	-1.181216

Solvent Phase

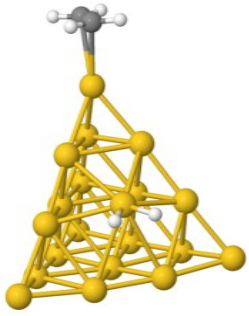
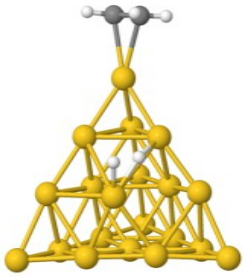
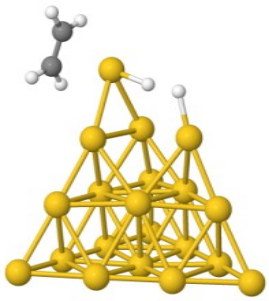
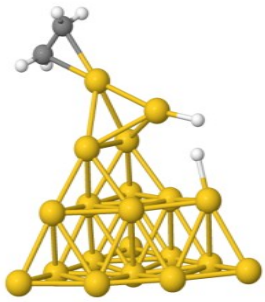
(Solvent Model: SMD, Solvent: Ethanol)

	Ethylene	H_2
E	-78.574839	-1.169031
U	-78.571802	-1.166671
H	-78.570858	-1.165727
G	-78.5957	-1.180522

6. Relative Energies of the TS of H_2 Dissociation on Au_{20} cluster

[DFT:B3LYP-D3(BJ)/def2-TZVP (Rh,C,H)+LANL2DZ(f) (Au)]

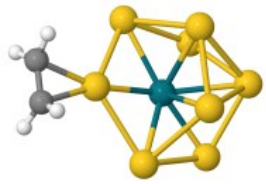
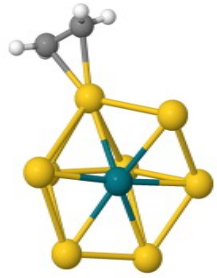
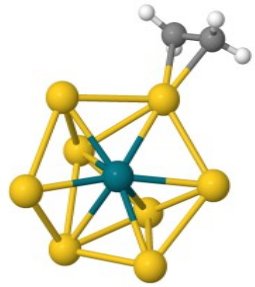
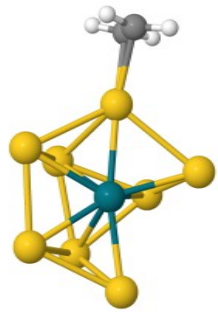
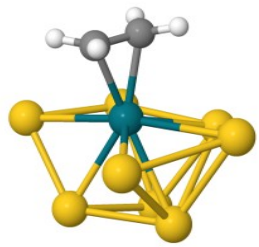
Lowest Energy structure is highlighted in bold font

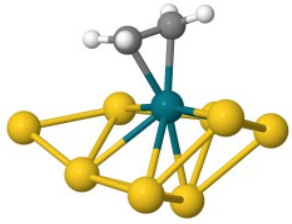
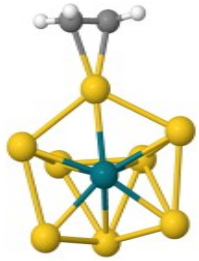
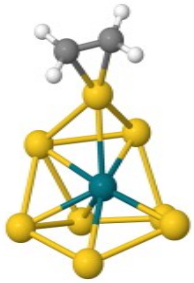
Transition States	Energy in a.u. (E+ZPE)	Relative Energies (kcal/mol)	Imaginary Freq (cm^{-1})
	-2790.123924	1.87	711.1644i
	-2790.122241	2.92	570.9132i
	-2790.125681	0.77	559.4148i
	**-2790.126909**	**0**	**893.8893i**

7. Relative Energies of the Ethylene Adsorbed Complex of Au_8Rh cluster

[ABCluster+Gaussian16]

Lowest Energy structure is highlighted in bold font

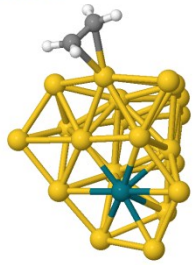
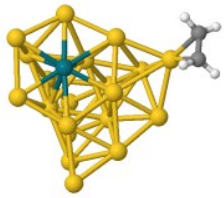
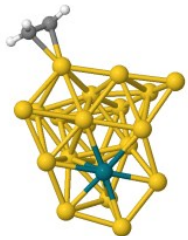
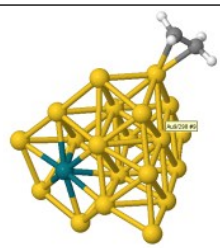
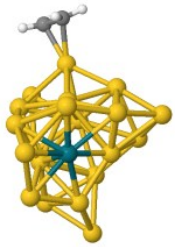
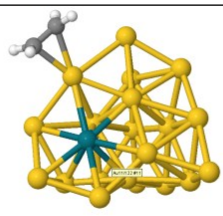
Geometries	Relative Energies (kcal/mol)
	10.43994662
	9.578814648
	11.61935167
	12.754329
	9.008345307

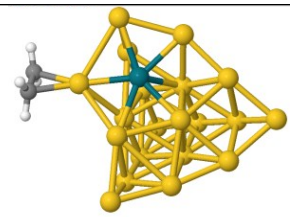
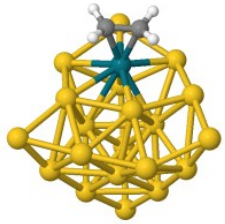
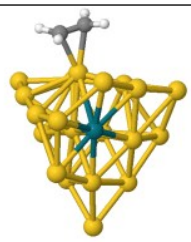
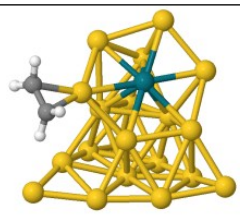
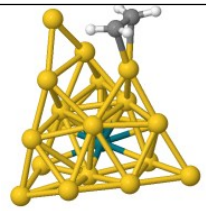
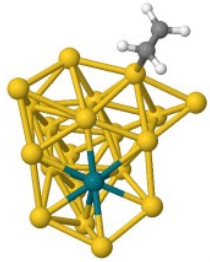
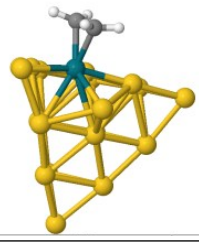
	**0**
	11.21103091
	14.69063661

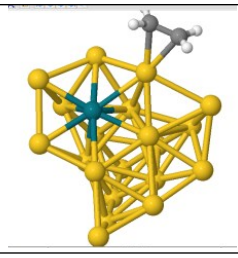
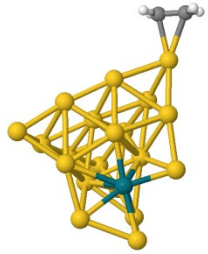
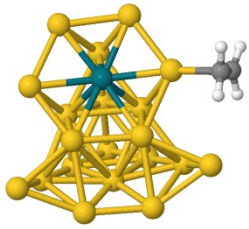
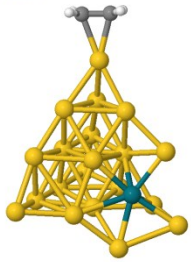
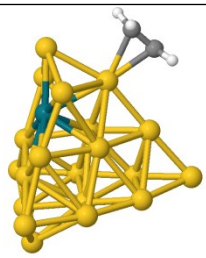
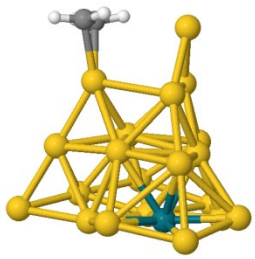
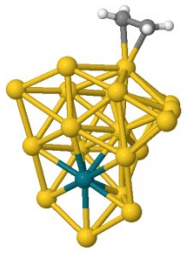
8. Relative Energies of the Ethylene Adsorbed Complex of $Au_{20}Rh$ cluster

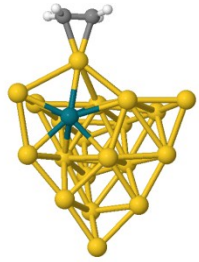
[ABCluster+Gaussian16]

Lowest Energy structure is highlighted in bold font

Geometries	Relative Energies (kcal/mol)
	15.66911295
	13.91296347
	10.74880704
	15.05911048
	16.87305364
	13.34036059

	5.179781295
	1.725778002
	17.77208722
	10.73719811
	13.79806639
	17.62173582
	**0**

	13.28407294
	15.49271989
	12.61696706
	14.77020488
	13.51499662
	14.42130932
	17.23067159

	4.468812465