

Supporting Information

Multireference Investigations of Ethylene Hydrogenation over Bimetallic Catalysts

Rishu Khurana,^{†,‡} Matthew R. Hermes,[†] Valay Agarawal,[†] Christopher Knight,[¶]
Laura Gagliardi,^{†,§} and Cong Liu^{*,‡,§}

[†]*Department of Chemistry, University of Chicago, Chicago, IL 60637, United States*

[‡]*Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL
60439, United States*

[¶]*Computational Science Division, Argonne National Laboratory, Lemont, IL 60439, United
States*

[§]*Pritzker School of Molecular Engineering, University of Chicago, Chicago, IL 60637,
United States*

E-mail: congliu@anl.gov

S1 Silsesquioxane (SSQ) as silica support

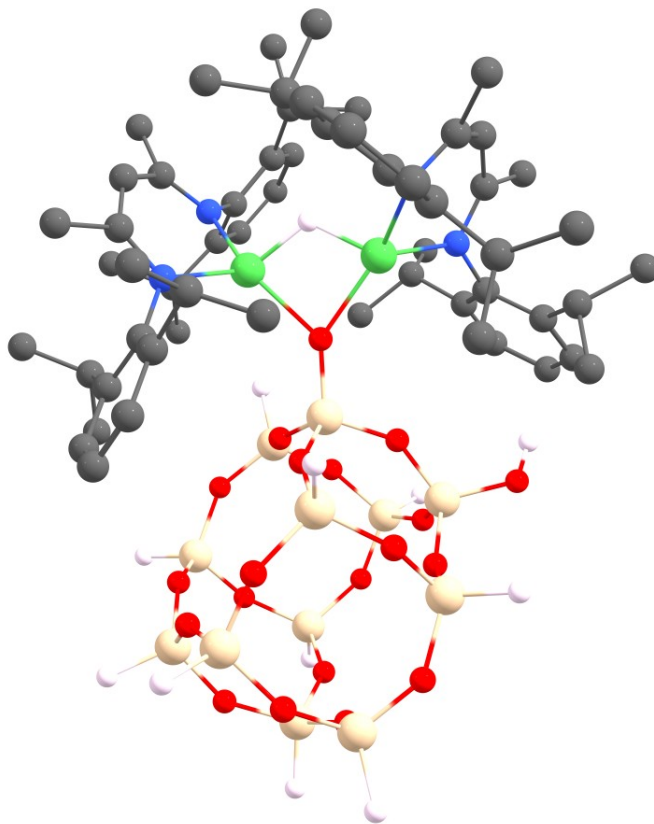


Figure S1: The optimized structure of Ni active catalyst on silsesquioxane cage as silica support.

S2 Natural charge

The NBO analysis was performed to compare the natural charges of the key atoms between the $\text{Si}(\text{OH})_3\text{O}$ and SSQ models. The calculated natural charges, reported in Table S1, show only minor differences between the two models, supporting the use of the smaller silanol model as a simplified representation of the SSQ-supported catalyst.

Table S1: Comparison of natural charges of key atoms demonstrating the electronic similarity between the $\text{Si}(\text{OH})_3\text{O}$ and SSQ support models.

Atoms	$\text{Si}(\text{OH})_3\text{O}$	SSQ
Ni_1	0.87	0.87
Ni_2	0.87	0.87
H	-0.21	-0.17
O-Ni	-1.24	-1.27
Si	2.41	2.53
O	-1.1	-1.3
O	-1.1	1.3
O	-1.1	-1.3

S3 Structure of intermediates and transition states

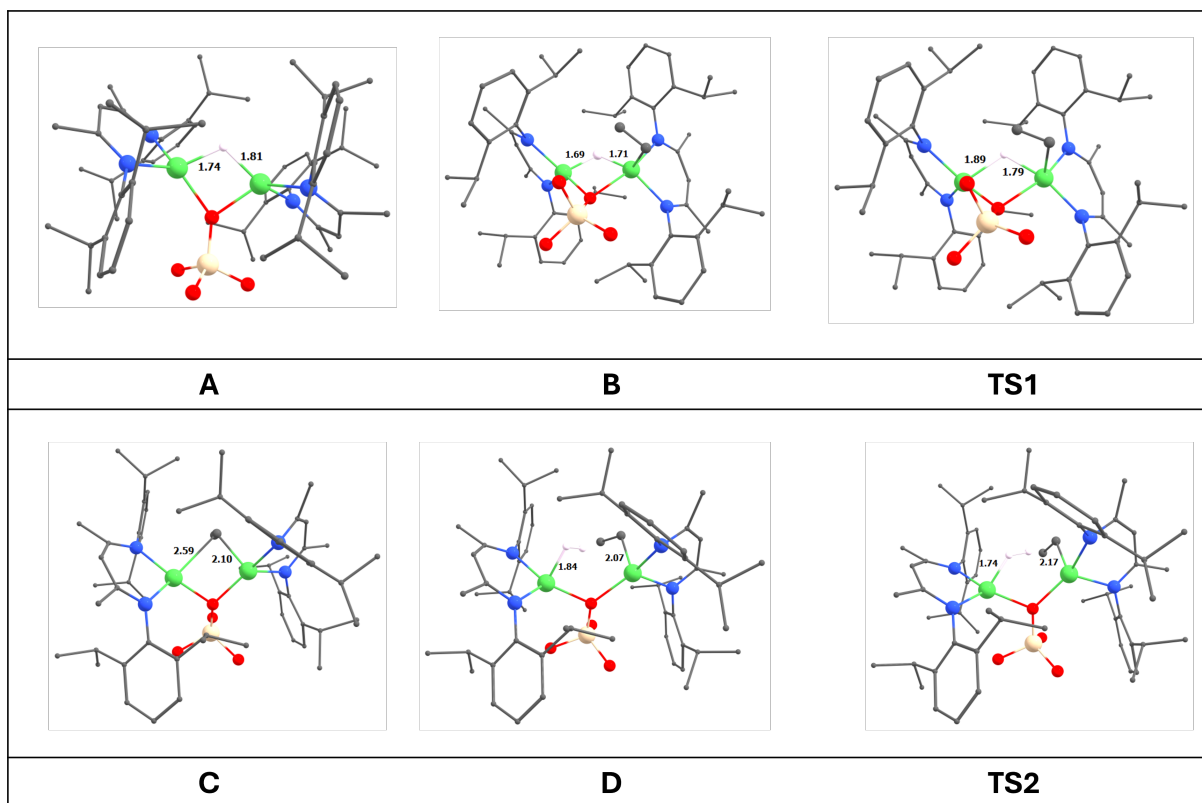


Figure S2: Optimized geometries of the intermediates and transition states involved in the catalytic cycle for silica-supported catalyst.

S4 LASSCF active space size for Fe catalysts

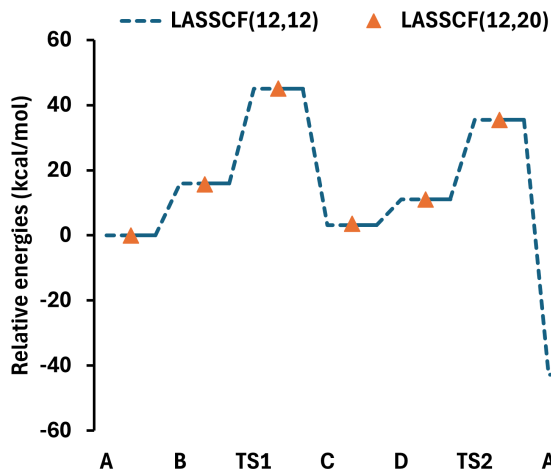


Figure S3: Comparison of reaction energy profile for unsupported Fe catalytic systems with LASSCF(12,12) vs LASSCF(12,20) with reduced basis set partition scheme.

S5 Comparison of MC-PDFT and NEVPT2

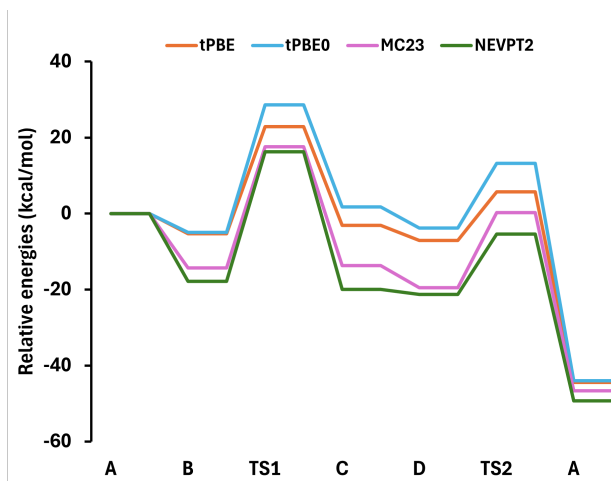


Figure S4: Comparison of reaction energy profiles obtained with three on-top MC-PDFT functionals, tPBE, tPBE0, MC23 and NEVPT2 for unsupported Ni catalyst with (4,4) active space and reduced basis set partition scheme.

S6 Spin-state energetics

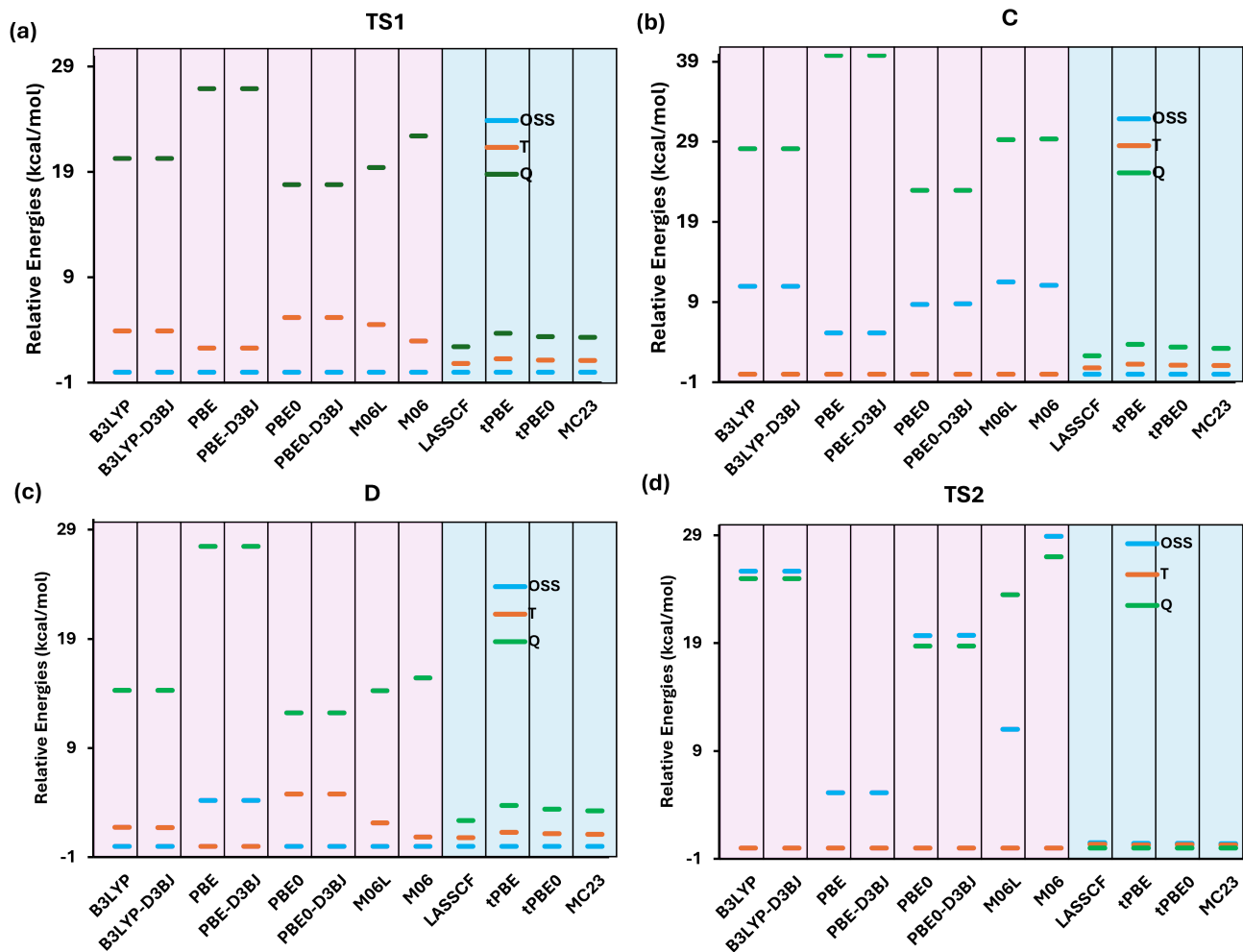


Figure S5: Spin-state energetics for intermediates, **C**, **D**, and transition states, **TS1** and **TS2** for unsupported Ni catalyst.

All DFT and multireference (MR) methods consistently predict open-shell singlet ground states for **A**, **TS1**. However, the energy gaps to higher excited states show significant functional dependence in DFT, whereas they remain consistent across different MC-PDFT functionals. For **D**, the ground-spin state from DFT remains Oss with most of the DFT functionals and MR methods, but changes to triplet with PBE and PBE-D3BJ.

For **B**, the ground-spin state analysis from the various methods is discussed in the main

manuscript, and **C** follows a similar trend.

In contrast, **TS2** exhibits markedly different behavior. None of the methods predict an open-shell singlet ground state. DFT methods favor a triplet ground state, while MR approaches predict a quintet ground state, with the triplet and open-shell singlet states lying within 0.5 kcal/mol.

S7 LASSCF computed barriers with tPBE and tPBE0 on-top functionals.

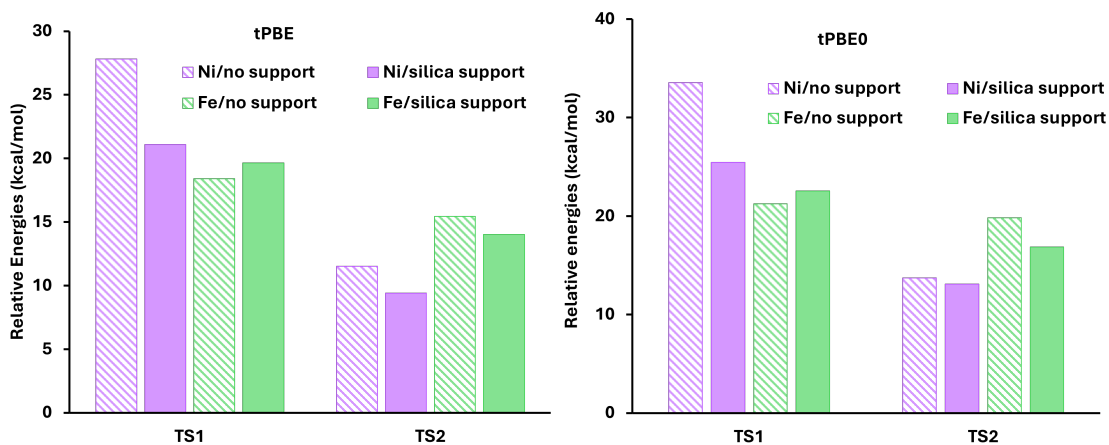


Figure S6: Computed transition state barriers (kcal/mol) for the two transition states with (a)tPBE and (b)tPBE0 on-top functionals for all the catalysts.

S8 CPU and GPU profiling

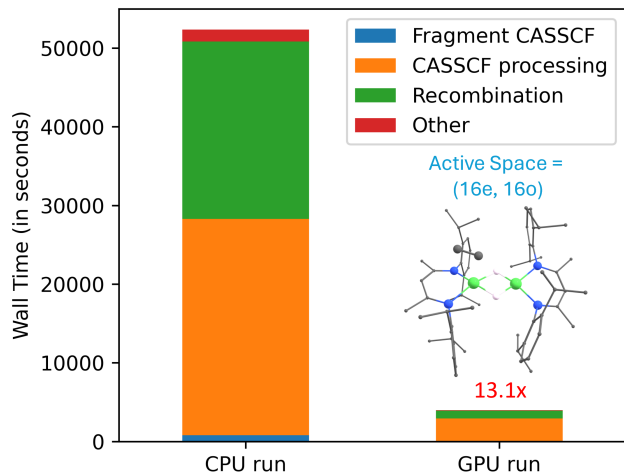


Figure S7: Calculation profile of LASSCF for the ethylene-bound species, **B**, of unsupported Ni catalyst with (16e,16o) active space with CPUs and GPUs resource utilization on 8x NVIDIA A100 GPUs on Sophia at ALCF.

S9 *N*-diagnostic

Table S2: *N*-diagnostic for different intermediates and transition states for all the studied catalysts.

	Ni/no support	Ni/silica support	Fe/no support	Fe/silica support
A	0.22	0.09	0.18	0.11
B	0.17	0.12	0.17	0.11
TS1	0.19	0.12	0.15	0.10
C	0.17	0.07	0.19	0.11
D	0.17	0.05	0.16	0.10
TS2	0.03	0.07	0.12	0.07

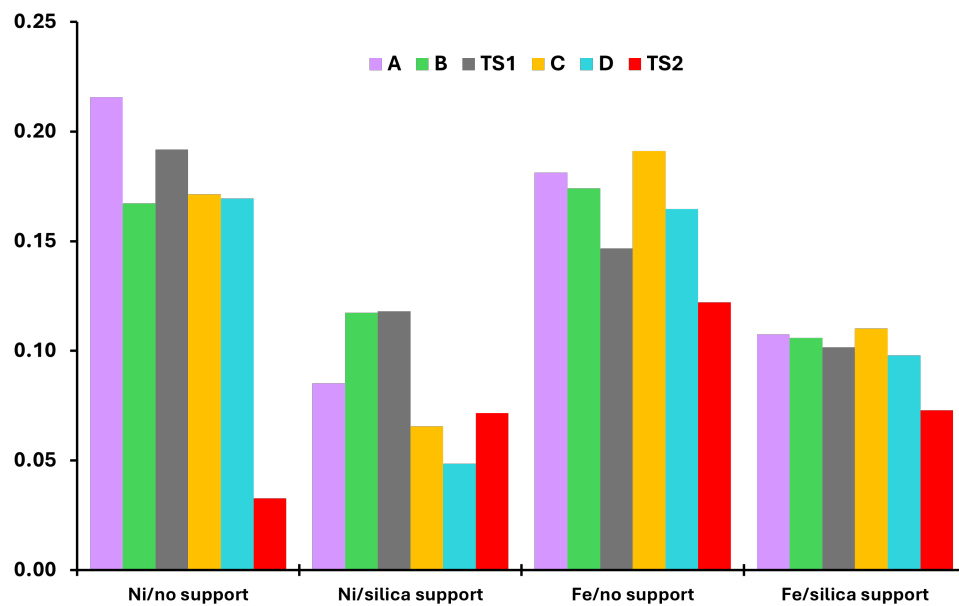


Figure S8: *N*-diagnostic for different intermediates and transition states for all the studied catalysts.

S10 Mulliken Charges

Table S3: Mulliken atomic charges on key atoms for all the catalytic systems obtained from MR methods.

		Ni/ no support	Ni/ silica support	Fe/ no support	Fe/ silica support
A	M	1.27	1.34	1.29	1.35
	M	1.28	1.34	1.3	1.37
	H	-0.61	-0.57	-0.62	-0.58
	H/O	-0.63	-1.18	-0.63	-1.18
	O-(Si)		-0.83		-0.83
B	M	1.24	1.33	1.28	1.36
	M	1.25	1.34	1.32	1.38
	H	-0.59	-0.59	-0.62	-0.59
	H/O	-0.59	-1.16	-0.63	-1.16
	O-(Si)		-0.83		-0.83
TS1	M	1.28	1.35	1.29	1.39
	M	1.29	1.37	1.32	1.39
	H	-0.37	-0.4	-0.36	-0.36
	H/O	-0.57	-1.15	-0.52	-1.16
	O-(Si)		-0.83		-0.82
C	M	1.25	1.33	1.29	1.38
	M	1.29	1.4	1.31	1.39
	C of ethyl	-0.77	-0.74	-0.79	-0.77
	H/O	-0.55	-1.16	-0.57	-1.16
	O-(Si)		-0.83		-0.83
D	M	1.28	1.32	1.3	1.39
	M	1.28	1.42	1.31	1.4
	C of ethyl	-0.78	-0.71	-0.79	-0.78
	H/O	-0.56	-1.15	-0.57	-1.16
	O-(Si)		-0.83		-0.83
TS2	M	1.27	1.38	1.29	1.41
	M	1.3	1.38	1.31	1.41
	C of ethyl	-0.62	-0.61	-0.63	-0.62
	H/O	-0.58	-1.16	-0.58	-1.16
	O-(Si)		-0.83		-0.83

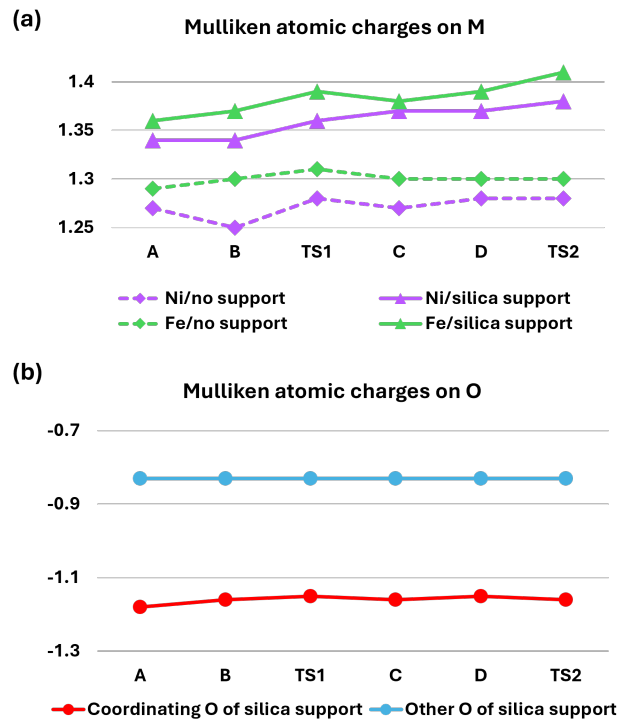


Figure S9: Mulliken atomic charges on key atoms for all the catalytic systems obtained from MR methods.

S11 Electronic Energies

S11.1 DFT electronic energies for unsupported Ni catalyst.

For **A**, **TS1** and **D**, the ground-state is open-shell singlet while for **B**, **C** and **TS2**, triplet is observed to be the ground state.

Table S4: Electronic energies obtained from single-point calculations with different DFT functionals on B3LYP optimized geometries for unsupported Ni catalyst.

	Spin	B3LYP	B3LYP-D3BJ	M06L	M06
A	OSS	-5495.601051	-5496.016472	-5497.048432	-5495.417142
	T	-5495.592497	-5496.007916	-5497.041749	-5495.410363
	Q	-5495.571123	-5495.986543	-5497.017816	-5495.385006
B	OSS	-5574.136780	-5574.581268	5575.650047	-5573.966296
	T	-5574.150462	-5574.594951	-5575.662294	-5573.981489
	Q	-5574.097891	-5574.542379	-5575.611897	-5573.924889
C	OSS	-5574.151842	-5574.593067	-5575.663934	-5573.983864
	T	-5574.169323	-5574.610544	-5575.682325	-5574.001569
	Q	-5574.124468	-5574.565702	-5575.635693	-5573.954758
TS1	OSS	-5574.131390	-5574.564225	-5575.634175	-5573.949853
	T	-5574.125181	-5574.558022	-5575.626997	-5573.945138
	Q	-5574.099082	-5574.531918	-5575.603230	-5573.914151
D	OSS	-5575.325186	-5575.766060	-5576.835768	-5575.15222
	T	-5575.322425	-5575.763316	-5576.832348	-5575.150878
	Q	-5575.302431	-5575.743316	-5576.813069	-5575.127663
TS2	OSS	-5575.281618	-5575.725264	-5576.814239	-5575.106646
	T	-5575.322512	-5575.766163	-5576.831809	-5575.152734
	Q	-5575.282697	-5575.726343	-5576.794354	-5575.109663
C₂H₄		-78.565598	-78.569543	-78.602199	-78.547131
C₂H₆		-79.798821	-79.804234	-79.844159	-79.784643
H₂		-1.172897	-1.173037	-1.171633	-1.170551

Table S5: Electronic energies obtained from single-point calculations with different DFT functionals on B3LYP optimized geometries for unsupported Ni catalyst.

	Spin	PBE	PBE-D3BJ	PBE0	PBE0-D3BJ
A	OSS	-5493.627202	-5493.883844	-5493.917303	-5494.153212
	T	-5493.625744	-5493.882383	-5493.905795	-5494.141684
	Q	-5493.57969	-5493.83616	-5493.891273	-5494.127169
B	OSS	-5572.11354	-5572.389206	-5572.413999	-5572.667864
	T	-5572.119628	-5572.395291	-5572.421969	-5572.675835
	Q	-5572.0479	-5572.323569	-5572.379094	-5572.63296
C	OSS	-5572.138019	-5572.411507	-5572.432237	-5572.683717
	T	-5572.146224	-5572.419703	-5572.446114	-5572.697757
	Q	-5572.082846	-5572.356323	-5572.409519	-5572.661156
TS1	OSS	-5572.110613	-5572.378562	-5572.406028	-5572.652124
	T	-5572.106971	-5572.374919	-5572.397767	-5572.643852
	Q	-5572.067757	-5572.335708	-5572.37767	-5572.623762
D	OSS	-5573.284381	-5573.557634	-5573.602911	-5573.854069
	T	-5573.291083	-5573.56435	-5573.595273	-5573.846425
	Q	-5573.247327	-5573.520591	-5573.583422	-5573.834581
TS2	OSS	-5573.289073	-5573.564389	-5573.564629	-5573.818065
	T	-5573.297263	-5573.572579	-5573.596047	-5573.849508
	Q	-5573.244516	-5573.519832	-5573.566178	-5573.819648
C₂H₄		-78.50040881	-78.50252102	-78.51224421	-78.51413765
C₂H₆		-79.73098361	-79.73407977	-79.75022662	-79.75284425
H₂		-1.165913725	-1.165970021	-1.168216101	-1.168282736

S11.2 Electronic energies from MR methods

The ground-states are highlighted in gray. All the intermediates and transition states consistently show open-shell singlet for all the catalysts except TS2 for unsupported Ni catalyst that is stabilized in quintet.

Table S6: Electronic energies from MR methods for unsupported Ni catalyst.

	Spin	LASSCF	tPBE	tPBE0	MC23
A	OSS	-5475.651430	-5490.722191	-5486.954501	-5491.034330
	T	-5475.649637	-5490.719375	-5486.951941	-5491.031870
	Q	-5475.646157	-5490.714024	-5486.947058	-5491.027173
B	OSS	-5553.719898	-5569.210575	-5565.337905	-5569.593493
	T	-5553.718763	-5569.208730	-5565.336238	-5569.591884
	Q	-5553.716515	-5569.205143	-5565.332986	-5569.588745
C	OSS	-5553.683915	-5569.204821	-5565.324595	-5569.590132
	T	-5553.682658	-5569.202783	-5565.322752	-5569.588376
	Q	-5553.680198	-5569.198852	-5565.319188	-5569.584974
D	OSS	-5554.830392	-5570.374914	-5566.488783	-5570.762818
	T	-5554.829122	-5570.372889	-5566.486947	-5570.761053
	Q	-5554.826617	-5570.368969	-5566.483381	-5570.757617
TS1	OSS	-5553.639158	-5569.166241	-5565.28447	-5569.542352
	T	-5553.637869	-5569.164244	-5565.282650	-5569.540567
	Q	-5553.635333	-5569.160380	-5565.279118	-5569.537099
TS2	OSS	-5554.783183	-5570.351005	-5566.459050	-5570.728315
	T	-5554.783453	-5570.351229	-5566.459285	-5570.728535
	Q	-5554.783995	-5570.351682	-5566.459760	-5570.728975
C₂H₄		-78.065121	-78.484058	-78.379324	-78.538811
H2		-1.132509	-1.165204	-1.157030	-1.165440
C₂H₄		-79.259787	-79.714171	-79.600575	-79.773560

Table S7: Electronic energies from MR methods for unsupported Fe catalyst.

		LASSCF	tPBE	tPBE0	MC23
A	OSS	-4986.718725	-5001.616108	-4997.891762	-5002.214785
	T	-4986.718536	-5001.615743	-4997.891442	-5002.214462
	Q	-4986.718156	-5001.615026	-4997.890809	-5002.213825
	S	-4986.717588	-5001.613958	-4997.889866	-5002.212875
	N	-4986.716829	-5001.612532	-4997.888606	-5002.211605
B	OSS	-5064.757923	-5080.091665	-5076.258229	-5080.757698
	T	-5064.757726	-5080.091295	-5076.257903	-5080.757373
	Q	-5064.757331	-5080.090566	-5076.257257	-5080.756732
	S	-5064.756734	-5080.089477	-5076.256291	-5080.755772
	N	-5064.755932	-5080.088015	-5076.254994	-5080.754482
TS1	OSS	-5064.710459	-5080.062340	-5076.224369	-5080.726181
	T	-5064.710310	-5080.062070	-5076.224130	-5080.725938
	Q	-5064.710011	-5080.061535	-5076.223654	-5080.725454
	S	-5064.709554	-5080.060726	-5076.222933	-5080.724722
	N	-5064.708930	-5080.059629	-5076.221955	-5080.723728
C	OSS	-5064.774059	-5080.110321	-5076.276256	-5080.779928
	T	-5064.773798	-5080.109866	-5076.275849	-5080.779520
	Q	-5064.773277	-5080.108969	-5076.275046	-5080.778712
	S	-5064.772495	-5080.107634	-5076.273849	-5080.777508
	N	-5064.771454	-5080.105854	-5076.272254	-5080.775902
D	OSS	-5065.893363	-5081.267515	-5077.423977	-5081.942064
	T	-5065.893155	-5081.267138	-5077.423642	-5081.941729
	Q	-5065.892735	-5081.266392	-5077.422977	-5081.941062
	S	-5065.892097	-5081.265274	-5077.42198	-5081.940061
	N	-5065.891231	-5081.263770	-5077.420635	-5081.938712
TS2	OSS	-5065.853994	-5081.250938	-5077.401702	-5081.919384
	T	-5065.853976	-5081.250841	-5077.401625	-5081.919297
	Q	-5065.853940	-5081.250652	-5077.401474	-5081.919126
	S	-5065.853885	-5081.250370	-5077.401249	-5081.918871
	N	-5065.853811	-5081.249994	-5077.400948	-5081.918530

Table S8: Electronic energies from MR methods for silica-supported Ni catalyst.

	Spin	LASSCF	tPBE	tPBE0	MC23
A	OSS	-6065.647167	-6082.211245	-6078.070225	-6082.632928
	T	-6065.647024	-6082.210966	-6078.06998	-6082.632686
	Q	-6065.646741	-6082.210426	-6078.069505	-6082.632215
B	OSS	-6143.699470	-6160.700504	-6156.450245	-6161.197983
	T	-6143.698944	-6160.699654	-6156.449477	-6161.197236
	Q	-6143.697900	-6160.697993	-6156.447970	-6161.195771
C	OSS	-6143.695695	-6160.703055	-6156.451215	-6161.198106
	T	-6143.695569	-6160.702837	-6156.451020	-6161.197910
	Q	-6143.695318	-6160.702410	-6156.450637	-6161.197522
D	OSS	-6144.803115	-6161.856249	-6157.592965	-6162.342642
	T	-6144.803080	-6161.856174	-6157.592901	-6162.342577
	Q	-6144.803010	-6161.856028	-6157.592774	-6162.342451
TS1	OSS	-6143.638005	-6160.666914	-6156.409687	-6161.158558
	T	-6143.637497	-6160.666093	-6156.408944	-6161.157828
	Q	-6143.636488	-6160.664482	-6156.407484	-6161.156393
TS2	OSS	-6144.789686	-6161.853297	-6157.587394	-6162.335516
	T	-6144.789543	-6161.853036	-6157.587163	-6162.335288
	Q	-6144.789257	-6161.852522	-6157.586706	-6162.334840

Table S9: Electronic energies from MR methods for silica-supported Fe catalyst.

		LASSCF	tPBE	tPBE0	MC23
A	OSS	-5576.715645	-5593.116551	-5589.016325	-5593.822947
	T	-5576.715613	-5593.116433	-5589.016228	-5593.822845
	Q	-5576.715543	-5593.116199	-5589.016035	-5593.822640
	S	-5576.715418	-5593.115847	-5589.015739	-5593.822325
	N	-5576.715214	-5593.115362	-5589.015325	-5593.821883
B	OSS	-5654.756904	-5671.600536	-5667.389628	-5672.379160
	T	-5654.756854	-5671.60041	-5667.389521	-5672.379048
	Q	-5654.756751	-5671.600163	-5667.389310	-5672.378828
	S	-5654.756595	-5671.599796	-5667.388995	-5672.378499
	N	-5654.756382	-5671.599301	-5667.388572	-5672.378055
TS1	OSS	-5654.707127	-5671.569231	-5667.353705	-5672.346827
	T	-5654.707082	-5671.569135	-5667.353622	-5672.346741
	Q	-5654.706992	-5671.568946	-5667.353458	-5672.346570
	S	-5654.706856	-5671.568664	-5667.353212	-5672.346314
	N	-5654.706670	-5671.568286	-5667.352882	-5672.345970
C	OSS	-5654.770959	-5671.613604	-5667.402943	-5672.396353
	T	-5654.770902	-5671.613481	-5667.402837	-5672.396240
	Q	-5654.770789	-5671.613243	-5667.402629	-5672.396019
	S	-5654.770618	-5671.61289	-5667.402322	-5672.395691
	N	-5654.770388	-5671.612419	-5667.401911	-5672.395251
D	OSS	-5655.880417	-5672.758512	-5668.538989	-5673.541666
	T	-5655.880373	-5672.758411	-5668.538902	-5673.541573
	Q	-5655.880283	-5672.758215	-5668.538732	-5673.541391
	S	-5655.880147	-5672.757925	-5668.53848	-5673.541121
	N	-5655.879966	-5672.757537	-5668.538144	-5673.540759
TS2	OSS	-5655.863000	-5672.756472	-5668.533104	-5673.523400
	T	-5655.862986	-5672.756430	-5668.533069	-5673.523363
	Q	-5655.862957	-5672.756349	-5668.533001	-5673.523291
	S	-5655.862914	-5672.756229	-5668.532900	-5673.523184
	N	-5655.862855	-5672.756068	-5668.532765	-5673.523041

S12 Gibbs free energies

Table S10: Gibbs free energies for unsupported Ni system computed using different DFT functionals, with thermal corrections taken from B3LYP for consistency across methods (matching the treatment applied to multireference electronic energies).

	B3LYP	B3LYP-D3BJ	M06L	M06
A	-5494.411586	-5494.827007	-5495.858967	-5494.227677
B	-5572.90928	-5573.353769	-5574.421112	-5572.740307
TS1	-5572.892268	-5573.325103	-5574.395053	-5572.710731
C	-5572.923169	-5573.36439	-5574.436171	-5572.755415
D	-5574.06796	-5574.508834	-5575.578542	-5573.894994
TS2	-5574.024609	-5574.468255	-5575.55723	-5573.849637
C₂H₄	-79.74394549	-79.7493588	-79.78928326	-79.72976723
H₂	-1.173027689	-1.173168518	-1.171764458	-1.170682485
C₂H₆	-78.53361336	-78.53755819	-78.57021382	-78.51514558

Table S11: Gibbs free energies for unsupported Ni system computed using different DFT functionals, with thermal corrections taken from B3LYP for consistency across methods (matching the treatment applied to multireference electronic energies).

	PBE	PBE-D3BJ	PBE0	PBE0-D3BJ
A	-5492.437736	-5492.694378	-5492.727838	-5492.963747
B	-5570.878446	-5571.154109	-5571.180787	-5571.434653
TS1	-5570.871491	-5571.139439	-5571.166906	-5571.413002
C	-5570.90007	-5571.173549	-5571.19996	-5571.451603
D	-5572.027155	-5572.300407	-5572.345684	-5572.596843
TS2	-5572.032064	-5572.307379	-5572.307619	-5572.561056
C₂H₄	-79.67610757	-79.67920373	-79.69535058	-79.69796821
H₂	-1.166044265	-1.166100561	-1.168346641	-1.168413276
C₂H₆	-78.46842333	-78.47053554	-78.48025873	-78.48215217

Table S12: Gibbs free energies for different catalytic systems computed using multireference (MR) methods. Thermal contributions are obtained from the DFT B3LYP functional for consistency across methods.

Gibbs energies (Eh)				
Ni/no support				
	LASSCF	tPBE	tPBE0	MC23
A	-5474.461965	-5489.532726	-5485.765036	-5489.844864
B	-5552.478716	-5567.969393	-5564.096723	-5568.352311
TS1	-5552.400036	-5567.927119	-5564.045348	-5568.30323
C	-5552.437761	-5567.958667	-5564.078441	-5568.343978
D	-5553.573166	-5569.117687	-5565.231557	-5569.505591
TS2	-5553.526174	-5569.093996	-5565.20204	-5569.471306
C₂H₄	-78.033135	-78.452073	-78.347338	-78.506825
C₂H₆	-79.204911	-79.659294	-79.545699	-79.718684
H₂	-1.132640	-1.165334	-1.157161	-1.165570
Fe/no support				
A	-4985.532007	-5000.42939	-4996.705044	-5001.028067
B	-5063.521563	-5078.855305	-5075.021869	-5079.521338
TS1	-5063.472969	-5078.824850	-5074.986880	-5079.488691
C	-5063.533367	-5078.869629	-5075.035564	-5079.539236
D	-5064.639931	-5080.014083	-5076.170545	-5080.688632
TS2	-5064.599551	-5079.996495	-5076.147259	-5080.664941
Ni/silica support				
A	-6064.421929	-6080.986006	-6076.844987	-6081.407689
B	-6142.419393	-6159.420427	-6155.170168	-6159.917906
TS1	-6142.359498	-6159.388408	-6155.131180	-6159.880051
C	-6142.413202	-6159.420561	-6155.168721	-6159.915613
D	-6143.507282	-6160.560415	-6156.297132	-6161.046809
TS2	-6143.483122	-6160.546733	-6156.280831	-6161.028952
Fe/silica support				
A	-5575.491091	-5591.891998	-5587.791771	-5592.598393
B	-5653.480017	-5670.323649	-5666.112741	-5671.102273
TS1	-5653.430502	-5670.292606	-5666.077080	-5671.070202
C	-5653.490502	-5670.333146	-5666.122485	-5671.115895
D	-5654.588230	-5671.466325	-5667.246801	-5672.249478
TS2	-5654.570471	-5671.463943	-5667.240575	-5672.230871