

Supplementary

Modifier Effect in Silica-Supported FePO_4 and Fe-Mo-O Catalysts for Propylene Glycol Oxidation

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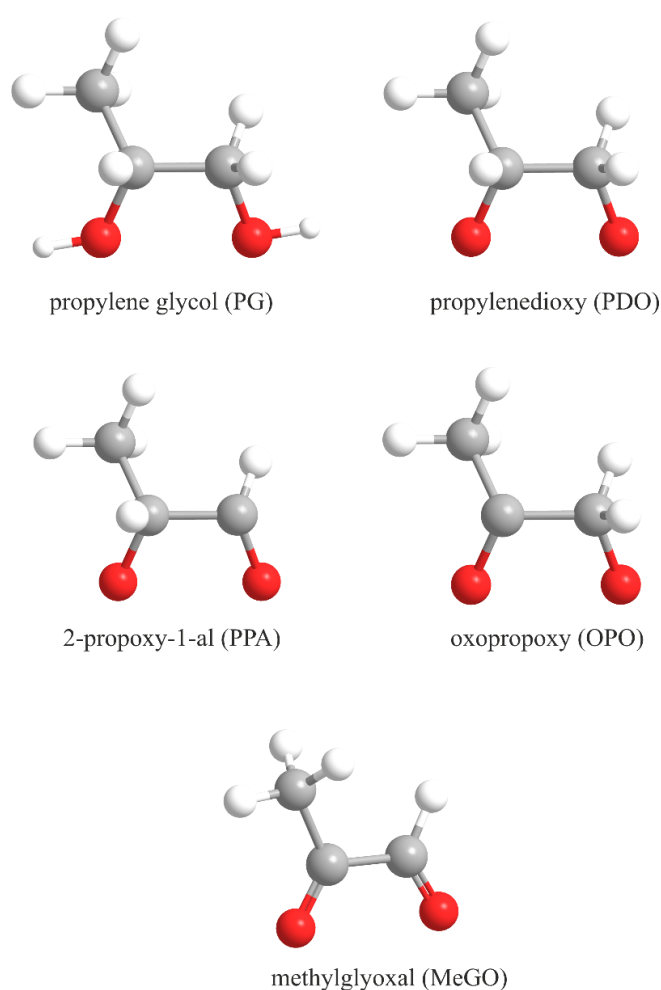


Figure S1. Geometries of substrates.

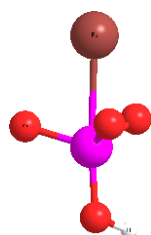


Figure S2. Calculated structure of iron phosphate (FePO_4H).

Table S1. DFT-optimized Cartesian coordinates for the main FePO₄-based models.

Element	X	Y	Z
FePO ₄ H			
Fe	−6.095141	−0.493745	−1.068161
P	−8.084016	0.186545	−1.289914
O	−9.583237	1.287554	−1.021465
O	−7.445038	0.695499	−1.450785
O	−7.445038	−0.584438	−2.504909
O	−7.793282	−0.825541	−0.119970
H	−9.660208	1.665827	−1.414896
FePO ₄ H+O ₂			
Fe	−0.482871	−1.860748	−0.138670
P	−2.501492	−1.065480	0.116941
O	−1.363558	−1.065480	0.305461
O	−4.002781	−0.574747	0.131324
O	−1.936945	−1.732065	−1.251926
O	−2.139232	−2.231328	1.067269
H	−4.137853	0.348205	−0.153127
O	0.803925	−2.807090	0.633210
O	1.235807	−1.598708	0.220019
FePO ₄ H+O			
Fe	1.488834	0.146322	0.331962
P	−0.567447	0.880776	0.102574
O	0.563688	1.939321	0.376228
O	−2.052713	1.383365	−0.063492
O	0.100124	0.100582	−1.089412
O	−0.251167	−0.137468	1.257528
H	−2.159088	2.352304	−0.025212
O	2.917369	−0.387401	0.487925
FePO ₄ H+PG			
C	1.571481	−0.495553	−0.029929
C	1.441737	0.962265	0.394182
C	2.098614	1.924530	−0.585656
O	0.800839	−1.270212	0.927829
O	0.003111	1.189987	0.463575
H	2.619547	−0.809562	0.004743
H	1.151500	−0.641255	−1.029846
H	1.860847	1.080216	1.402027
H	1.961805	2.961124	−0.260028
H	3.176075	1.737718	−0.641895
H	1.666148	1.815342	−1.584078
H	0.650792	−2.172383	0.585255
H	−0.213111	2.079279	0.787550
Fe	−1.068256	−0.497643	0.879737
P	−2.723857	−1.451155	−0.118861
O	−3.114542	−0.079440	0.501274
O	−3.913531	−2.197056	−0.905439
O	−1.451781	−1.123464	−0.993036
O	−2.086522	−2.259924	1.056698
H	−4.699197	−1.626212	−0.961303
FePO ₄ H+O+PG			
C	2.324294	0.835031	0.133313
C	2.401245	2.308005	0.548118
C	1.210433	3.157593	0.115396
O	1.412605	0.139719	1.044258
O	2.534716	2.248188	1.988590
H	3.296713	0.346316	0.234695

H	1.929450	0.706096	−0.873623
H	3.326143	2.716190	0.118977
H	1.344825	4.192215	0.453369
H	1.126606	3.177358	−0.974931
H	0.261669	2.784894	0.509003
H	1.475623	0.603476	1.911025
H	2.280455	3.105016	2.366528
Fe	−0.145572	−0.821914	0.544418
P	−1.859385	0.646332	−0.581660
O	−2.048805	2.101522	−0.791765
O	−3.057556	−0.236502	−1.215859
O	−0.479385	−0.020592	−1.082337
O	−1.658058	0.123250	0.937200
H	−3.728278	0.343862	−1.614928
O	−0.120837	−2.356057	0.753114
FePO ₄ H+PDO			
C	−3.681492	−2.700196	−0.901429
C	−2.850783	−1.416872	−0.902028
C	−2.114959	−1.152360	−2.219511
O	−4.993384	−2.343711	−1.373071
O	−3.804839	−0.356335	−0.659984
H	−3.790314	−3.100634	0.114714
H	−3.293671	−3.494102	−1.549744
H	−2.136616	−1.378783	−0.069804
H	−1.670267	−0.154039	−2.206564
H	−1.315347	−1.888218	−2.353283
H	−2.801967	−1.219488	−3.068841
Fe	−5.438581	−0.689082	−1.123316
P	−7.558075	0.703565	−1.322407
O	−7.871917	2.126155	−1.096107
O	−8.823595	−0.174504	−1.801731
O	−6.348381	0.308550	−2.329083
O	−6.871095	−0.176410	−0.144345
H	−9.617118	0.382964	−1.884165
FePO ₄ H+O+PDO			
C	−0.459017	0.888779	−2.332791
C	−0.186257	−0.590793	−2.574791
C	1.166262	−0.777661	−3.286328
O	−0.834161	1.395460	−1.288915
O	−0.193735	−1.328856	−1.378071
H	−1.770602	1.049327	0.182562
H	−0.298563	1.533408	−3.221856
H	−0.986433	−0.908662	−3.266889
H	1.297519	−1.834711	−3.528071
H	1.212523	−0.198469	−4.214650
H	1.984729	−0.468783	−2.629873
Fe	−1.586357	−2.300316	−0.917369
P	−2.864439	−0.771947	0.582904
O	−2.449154	0.737970	0.840092
O	−4.178908	−0.915679	1.466591
O	−3.049004	−1.064356	−0.939679
O	−1.805981	−1.836768	0.954188
H	−4.570118	−0.065648	1.735070
O	−1.672805	−3.747596	−1.481024
FePO ₄ H+OPO			
C	1.542085	−1.130946	−0.870611
C	1.488932	0.313012	−1.298646

C	2.492617	0.915020	−2.230360
O	0.552659	−1.385564	0.078405
O	0.568168	0.998099	−0.814370
H	2.546435	−1.363884	−0.477807
H	1.410416	−1.764910	−1.765246
H	3.342630	1.270269	−1.633697
H	2.873304	0.177721	−2.942012
H	2.061902	1.772015	−2.751285
Fe	−0.583501	−0.046117	0.472423
P	−2.675754	0.334950	1.834458
O	−2.957288	0.870837	3.182499
O	−4.022535	−0.054057	1.020191
O	−1.807389	1.242311	0.802493
O	−1.687243	−0.918007	1.647566
H	−4.806438	0.183751	1.544597
FePO ₄ H+O+OPO			
C	0.429744	−0.875519	−1.439907
C	0.538447	0.631384	−1.500067
C	0.797175	1.326431	−2.798945
O	0.152702	−1.322695	−0.136550
O	0.364844	1.270170	−0.451957
H	1.363923	−1.329700	−1.805143
H	−0.380036	−1.173523	−2.122704
H	1.224585	2.315283	−2.624559
H	1.439144	0.734735	−3.456827
H	−0.175411	1.448567	−3.292323
Fe	−0.210733	−0.047964	1.049385
P	−3.049414	0.109326	−0.177905
O	−2.066401	0.114525	1.046466
O	−4.264217	1.042623	0.316737
O	−2.426106	0.581480	−1.492121
O	−3.589347	−1.281161	−0.569067
H	−4.069315	1.489157	1.158112
O	0.780017	0.504382	2.124575
FePO ₄ H+PPA			
C	1.403431	−1.568002	0.097462
C	1.909997	−0.198159	0.415298
C	2.877300	0.313549	−0.672220
O	0.180347	−1.745703	−0.006756
O	0.814958	0.669622	0.583675
H	2.470435	−0.277329	1.365423
H	2.076472	−2.425757	−0.050585
H	3.204045	1.316504	−0.389559
H	3.757210	−0.331980	−0.764386
H	2.368443	0.375007	−1.638041
Fe	−0.799962	−0.077288	0.331791
P	−2.887458	0.515553	0.083466
O	−2.015467	1.644969	0.670440
O	−4.423540	0.816747	−0.203274
O	−2.010712	0.061182	−1.171443
O	−2.597719	−0.713136	1.007749
H	−4.623280	1.768522	−0.256242
FePO ₄ H+O+PPA			
C	1.609983	−1.503286	0.047330
C	1.807717	−0.027721	0.221455
C	2.327718	0.645560	−1.060145
O	0.520372	−2.004647	0.321531

O	0.588270	0.561062	0.633218
H	2.557785	0.098958	1.023002
H	2.426597	−2.144590	−0.319546
H	2.430660	1.716696	−0.874113
H	3.306992	0.245028	−1.341547
H	1.627520	0.498995	−1.887044
Fe	−0.734357	−0.531966	1.064178
P	−3.011003	0.284988	0.259670
O	−1.937511	0.884703	1.284660
O	−2.967912	1.245770	−1.039503
O	−2.005902	−0.992051	−0.081719
O	−4.386832	−0.058399	0.642759
H	−2.130534	1.735796	−1.110937
O	−0.755263	−1.181596	2.489952
FePO ₄ H+MeGO			
C	2.337906	−1.972785	1.203490
C	2.664092	−0.780015	2.008821
C	3.932418	−0.622316	2.785457
O	1.215642	−1.958747	0.647581
O	1.751225	0.083621	2.016184
H	2.986921	−2.850548	1.119227
H	3.874743	0.266563	3.415006
H	4.115610	−1.504814	3.408462
H	4.785366	−0.525374	2.102416
Fe	0.229903	−0.317709	0.864067
P	−1.880250	0.062573	1.036549
O	−0.930815	1.310499	1.088656
O	−3.447937	0.330917	1.174734
O	−1.432512	−0.657125	−0.266828
O	−1.209096	−0.846075	2.140634
H	−3.658917	1.024335	1.824543
FePO ₄ H+O+MeGO			
Fe	1.004139	−1.262654	0.121720
P	−1.447555	−0.768061	−0.161707
O	−2.334925	0.412828	−0.186552
O	−2.245311	−2.160842	−0.374626
O	−0.186115	−0.822137	−1.181348
O	−0.489247	−1.001547	1.126983
H	−3.196208	−1.989040	−0.486608
O	1.688913	−2.659747	0.103141
C	3.363854	0.342843	0.556816
O	2.144094	0.205708	0.385499
C	3.876447	1.786460	0.736094
O	3.138527	2.739675	0.712801
C	4.359987	−0.765292	0.602090
H	4.970932	1.874083	0.886911
H	3.893072	−1.741139	0.466409
H	5.118119	−0.602245	−0.175248
H	4.891578	−0.735192	1.562324
FePO ₄ H+HA			
C	1.528555	−1.175981	−0.852258
C	1.514359	0.324060	−0.527125
C	1.317957	1.305725	−1.642048
O	0.941786	−1.806070	0.323467
O	1.805338	0.678550	0.651419
H	2.549918	−1.550162	−0.986546
H	0.925221	−1.383329	−1.737200

H	1.468848	2.322398	−1.276999
H	2.021951	1.093326	−2.457281
H	0.301546	1.199411	−2.035566
Fe	0.020505	−0.144050	1.004134
P	−2.102991	0.262157	0.862599
O	−1.320872	1.449246	1.472172
O	−3.680042	0.465766	0.681508
O	−1.316545	−0.044269	−0.478146
O	−1.653807	−0.980934	1.704457
H	−3.974475	1.330337	1.018360
H	0.229749	−2.417282	0.060053
FePO ₄ H+O+HA			
C	0.037142	−0.523879	−2.236572
C	0.763427	0.603409	−1.524527
C	1.790215	1.379926	−2.291718
O	−0.323107	−1.549415	−1.361910
O	0.566987	0.897862	−0.332406
H	0.705112	−0.894426	−3.028603
H	−0.823693	−0.051935	−2.737729
H	2.013404	2.327251	−1.800121
H	2.706611	0.778662	−2.348704
H	1.452880	1.545830	−3.320115
Fe	−0.831383	0.596270	0.909875
P	−2.945497	−0.494955	0.080650
O	−2.200970	0.882542	−0.296309
O	−4.370904	−0.189985	0.753431
O	−3.083898	−1.474446	−1.030273
O	−1.879642	−0.861484	1.239032
H	−4.319114	0.421740	1.509022
O	−0.605449	1.474720	2.172243
H	−1.294521	−1.721887	−1.410065
FePO ₄ H+FD			
Fe	0.218522	−1.058340	0.549046
P	−1.665241	−0.278368	−0.105437
O	−0.888688	0.523798	1.017000
O	−3.045778	0.350110	−0.609484
O	−0.507158	−0.398324	−1.178436
O	−1.769405	−1.704915	0.475524
H	−2.955040	1.248384	−0.972019
C	2.117778	0.906638	0.053598
O	1.951329	−0.231800	0.502787
H	3.130441	1.330079	0.052160
H	1.268440	1.480438	−0.335139

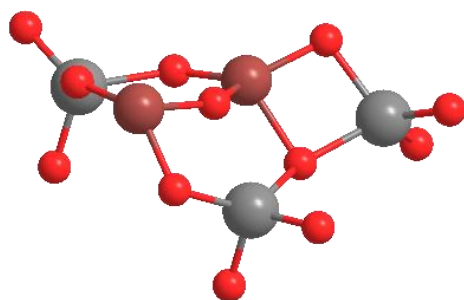


Figure S3. Calculated structure of iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$).

Table S2. DFT-optimized Cartesian coordinates for the main $\text{Fe}_2(\text{MoO}_4)_3$ -based models.

Element	X	Y	Z
$\text{Fe}_2(\text{MoO}_4)_3$			
Mo	0.174485	−1.731996	0.936697
Fe	3.398447	−1.877739	0.543483
O	−0.466200	−1.326343	−0.602810
O	1.982887	−1.023392	1.068315
O	−0.848912	−1.082973	2.145065
O	0.307871	−3.625066	1.084238
Mo	5.826907	−1.380550	−0.624543
O	6.383842	0.183185	−1.034499
O	7.094858	−2.494315	−0.899858
O	5.064077	−1.508090	1.123159
O	4.029335	−1.862803	−1.292628
Mo	3.030129	−3.548249	−2.123999
O	2.190309	−2.734460	−3.367425
O	2.830207	−3.440750	0.085816
O	1.781780	−4.890835	−1.487876
O	4.320574	−4.394877	−2.857430
Fe	1.507505	−4.610568	0.241806
$\text{Fe}_2(\text{MoO}_4)_3 + \text{O}_2$			
Mo	−2.488270	0.675963	0.963609
Fe	0.149837	0.162428	2.265839
O	−2.529429	1.850446	−0.268175
O	−1.245758	1.113630	2.485388
O	−3.986794	0.795167	1.781313
O	−2.622879	−1.219138	0.301480
Mo	2.260370	1.241070	0.079654
O	1.317726	2.506462	−0.573796
O	3.863122	1.818909	0.187315
O	1.678189	0.866436	1.896537
O	2.225493	−0.292126	−1.071862
Mo	0.946004	−1.236269	−2.136796
O	−0.006922	−0.143137	−3.039873
O	−0.381399	−0.188185	0.558195
O	−0.208133	−2.362786	−1.056675
O	1.751634	−2.245699	−3.253955
Fe	−1.050928	−1.871904	0.363499
O	−0.542208	−2.410792	1.918030
O	0.018945	−1.470496	2.796083
$\text{Fe}_2(\text{MoO}_4)_3 + \text{O}$			
Mo	−2.678957	0.451253	1.025184
Fe	0.504555	0.273838	1.266690
O	−2.692653	0.908153	−0.633724
O	−0.922074	0.992646	1.799728
O	−4.043579	1.086332	1.839257
O	−2.501575	−1.392615	1.210151
Mo	2.587862	1.597827	0.123803
O	2.559277	3.300785	0.029417
O	4.119602	1.071145	−0.406475
O	2.050658	0.904676	1.846872
O	0.974140	0.670310	−0.544246
Mo	0.433467	−1.107208	−1.593380
O	0.034393	−0.355297	−3.075460
O	0.283929	−1.348552	0.697239
O	−1.030138	−2.260647	−1.215636
O	1.855748	−2.007586	−1.888040

Fe	−1.206457	−2.471774	0.566687
O	−1.174199	−3.912289	1.118934
Fe ₂ (MoO ₄) ₃ +PG			
Mo	−3.662732	2.009633	−9.536199
Fe	−0.616234	1.511831	−9.876891
O	−3.647085	2.463537	−11.231549
O	−1.909396	2.261666	−8.860418
O	−4.834389	2.886279	−8.644615
O	−3.947484	0.159412	−9.455362
Mo	0.939267	3.070825	−11.507449
O	1.190786	4.740390	−11.201487
O	1.965365	2.598412	−12.794958
O	1.133402	1.996013	−9.923537
O	−0.917764	2.556477	−11.612153
Mo	−2.174680	1.242798	−12.787613
O	−2.986793	2.153251	−13.982938
O	−1.436962	0.299920	−10.749843
O	−3.263446	−0.244905	−12.273474
O	−0.864255	0.526642	−13.639409
Fe	−2.813997	−0.785429	−10.584845
C	−0.853096	−0.436949	−7.453808
C	−1.261101	−1.824378	−7.973519
C	−1.519402	−2.803071	−6.830127
O	−0.034899	0.259499	−8.427467
O	−2.454137	−1.774090	−8.819076
H	−0.259222	−0.554868	−6.544041
H	−1.724889	0.182591	−7.225067
H	−0.475986	−2.198214	−8.633551
H	−1.872702	−3.756907	−7.228500
H	−0.599213	−2.983832	−6.266287
H	−2.273536	−2.418406	−6.133097
H	0.765906	0.645529	−8.030176
H	−3.199126	−1.411256	−8.295643
Fe ₂ (MoO ₄) ₃ +O+PG			
Mo	−2.684097	1.793588	−1.037340
Fe	−0.154765	0.920673	0.656558
O	−3.553059	3.130982	−1.655762
O	−1.187288	2.282451	−0.080869
O	−3.668620	0.871549	0.098288
O	−2.057526	0.580279	−2.400278
Mo	2.250627	2.286917	−1.041124
O	1.221190	3.111780	−2.142163
O	3.632235	3.257538	−0.750923
O	1.373469	1.908193	0.569921
O	2.702060	0.549091	−1.807794
Mo	2.046782	−1.219698	−1.902517
O	3.122305	−2.108532	−2.882769
O	0.045709	−0.062407	−0.713525
O	0.333838	−1.355546	−2.781446
O	2.060739	−1.956933	−0.318396
Fe	−1.074139	−0.773385	−1.871365
O	−1.872680	−1.917982	−1.151574
C	−1.412515	−1.221292	2.052143
C	−0.010095	−1.229980	2.655054
C	0.533804	−2.625857	2.916888
O	−1.645172	0.153018	1.628829
O	0.869325	−0.472986	1.763765

H	−2.166350	−1.482944	2.800013
H	−1.497968	−1.876044	1.177607
H	−0.020757	−0.640675	3.576432
H	1.532828	−2.563341	3.355771
H	−0.114844	−3.154285	3.622730
H	0.592436	−3.212842	1.995049
H	−2.556769	0.306407	1.214537
H	1.332295	−1.077234	1.124657
Fe ₂ (MoO ₄) ₃ +PDO			
Mo	−3.012801	2.739331	−0.612618
Fe	−0.312182	2.240176	0.777085
O	−2.588751	2.788664	−2.273617
O	−1.581826	3.397927	0.516825
O	−4.380558	3.738644	−0.392402
O	−3.454214	0.935671	−0.074274
Mo	1.908883	2.750462	−1.598216
O	1.695149	4.308695	−2.273635
O	3.584879	2.399288	−1.609482
O	1.269171	2.687526	0.223984
O	0.891401	1.463168	−2.551151
Mo	0.084829	−0.269283	−2.225241
O	0.080073	−0.966608	−3.783610
O	−0.800397	1.013497	−0.425345
O	−1.712787	−0.914836	−1.609653
O	1.208144	−1.171046	−1.294787
Fe	−2.130205	−0.194048	−0.122102
C	−0.253031	0.322513	2.880387
C	−0.313992	−0.842745	1.885623
C	−0.000859	−2.168141	2.586828
O	−0.498057	1.627550	2.369284
O	−1.623709	−0.984706	1.306874
H	0.739164	0.322930	3.349132
H	−1.010652	0.181515	3.662479
H	0.412771	−0.680198	1.082312
H	−0.047935	−2.985870	1.864439
H	1.007928	−2.140122	3.010586
H	−0.719638	−2.366852	3.386993
Fe ₂ (MoO ₄) ₃ +O+PDO			
Mo	−2.409227	1.807421	0.211632
Fe	0.675831	1.711800	0.063047
O	−2.894177	2.380199	−1.324856
O	−0.627023	2.745369	0.328399
O	−3.396708	2.627773	1.338897
O	−3.127051	−0.063881	0.138109
Mo	2.538633	2.894692	−1.652813
O	2.262379	4.283517	−2.619846
O	4.182171	2.434743	−1.834751
O	2.030996	3.096714	0.105251
O	1.152932	1.408466	−1.677903
Mo	−0.122527	−0.003421	−2.564743
O	−0.491187	0.869946	−3.985585
O	−0.699145	0.301489	−0.548953
O	−1.752875	−1.110008	−2.248459
O	1.055436	−1.182718	−2.952799
Fe	−1.954329	−1.080713	−0.551514

C	0.867462	−0.092756	2.227116
C	−0.571100	0.033727	2.748833
C	−0.894715	−0.768419	3.980986
O	1.361455	0.974863	1.473037
O	−1.407387	0.742041	2.207597
H	0.941054	−1.047348	1.683330
H	1.537495	−0.184060	3.093798
H	−0.289000	−2.180879	0.573609
H	−1.971652	−0.922833	4.055721
H	−0.366079	−1.726794	3.989625
H	−0.556871	−0.201177	4.857808
O	−1.229987	−2.344656	0.372224
Fe ₂ (MoO ₄) ₃ +OPO			
Mo	−2.916784	2.426135	−0.303774
Fe	0.089997	1.933769	0.589376
O	−2.885907	3.090449	−1.885046
O	−1.312843	2.944779	0.691944
O	−4.331242	2.994290	0.477706
O	−2.887897	0.539657	−0.352564
Mo	1.875323	2.114273	−1.969587
O	0.747672	2.901093	−2.984483
O	3.383999	2.853897	−2.278332
O	1.556822	2.569373	−0.078415
O	2.085263	0.276256	−2.485063
Mo	1.322031	−1.464967	−2.238151
O	1.799228	−2.543139	−3.480272
O	−0.172949	0.945110	−0.856840
O	−0.542035	−1.355409	−2.153024
O	1.866735	−2.080630	−0.707523
Fe	−1.388176	−0.332633	−0.891894
C	0.724600	−0.538045	1.849995
C	−0.350001	−1.583049	1.553920
C	−0.343635	−2.831196	2.376355
O	0.279161	0.795099	1.901049
O	−1.197000	−1.460664	0.654406
H	1.506986	−0.705509	1.095046
H	1.162979	−0.758140	2.830946
H	−1.049133	−3.563476	1.984172
H	0.671158	−3.246729	2.386613
H	−0.596350	−2.578593	3.413439
Fe ₂ (MoO ₄) ₃ +O+OPO			
Mo	−2.904336	2.358035	−0.242391
Fe	0.403554	1.749076	0.032619
O	−3.824589	3.283448	−1.351455
O	−1.076427	2.709726	−0.413351
O	−3.484937	2.697538	1.336901
O	−3.080173	0.445942	−0.636051
Mo	2.421537	2.973625	−1.435910
O	2.158070	4.272327	−2.521920
O	4.115157	2.767756	−1.262695
O	1.553177	3.202718	0.223603
O	1.388611	1.335550	−1.748099
Mo	0.390811	−0.287562	−2.481139
O	0.041880	0.291465	−4.052254
O	−0.326327	0.065527	−0.485749

O	−1.315074	−1.311329	−2.153477
O	1.591455	−1.492948	−2.632511
Fe	−1.893516	−0.800300	−0.613214
C	0.931392	−0.233826	2.059671
C	−0.518997	−0.141879	2.878399
C	−0.650019	−1.218993	3.928116
O	1.282638	0.937189	1.544576
O	−1.313872	0.695422	2.590496
H	0.625527	−0.994609	1.318999
H	1.657639	−0.606040	2.794173
H	−0.068068	−0.915631	4.805170
H	−1.701646	−1.324528	4.197461
H	−0.246021	−2.162272	3.552834
O	−1.884445	−1.826422	0.574199
Fe ₂ (MoO ₄) ₃ +PPA			
Mo	−2.651794	2.296464	−0.653183
Fe	0.237873	1.702631	0.431373
O	−2.161538	2.803355	−2.217969
O	−1.295103	2.623634	0.630583
O	−4.086553	3.133888	−0.239074
O	−2.950523	0.367252	−0.643071
Mo	2.198816	2.256402	−2.257822
O	1.703889	3.626112	−3.158549
O	3.912294	2.206148	−2.292598
O	1.626680	2.392195	−0.452059
O	1.445633	0.650526	−3.006981
Mo	0.831738	−1.075851	−2.469855
O	1.098948	−2.078822	−3.825750
O	−0.185609	0.433837	−0.739317
O	−1.041658	−1.490104	−2.029452
O	1.822916	−1.690344	−1.199327
Fe	−1.566757	−0.677303	−0.591840
C	−0.025237	−0.376763	2.551637
C	−0.036054	−1.558110	1.582683
C	0.107647	−2.887878	2.315610
O	0.074371	0.806427	2.221107
O	−1.286811	−1.551522	0.890102
H	−0.122976	−0.584631	3.629856
H	0.792177	−1.421185	0.873810
H	0.132316	−3.702769	1.589441
H	1.044117	−2.906374	2.884691
H	−0.730800	−3.052218	2.998954
Fe ₂ (MoO ₄) ₃ +O+PPA			
Mo	−2.916566	1.176285	−0.331708
Fe	0.140190	0.980784	0.151559
O	−2.559127	1.731903	−1.937173
O	−1.459646	1.611491	0.773466
O	−4.346065	1.907450	0.258840
O	−3.130795	−0.742324	−0.502233
Mo	1.719678	3.049088	−0.769966
O	1.273095	4.687814	−0.529681
O	3.298253	3.011173	−1.437101
O	1.554825	2.010331	0.798542
O	0.363016	1.919569	−1.613292
Mo	−0.314649	0.525545	−2.991445
O	−0.907280	1.489346	−4.271917
O	−0.486697	−0.314479	−0.980535

O	−1.615334	−1.034402	−2.986489
O	1.133582	−0.160112	−3.580160
Fe	−1.814486	−1.500927	−1.358626
C	0.615478	−1.218182	3.809329
C	0.340810	0.000909	2.890103
C	0.179274	1.333065	3.536555
O	0.681704	−2.340597	3.372549
O	0.296577	−0.236542	1.680955
H	0.742138	−0.982906	4.884594
H	−0.224555	−2.684460	−0.287449
H	−0.257066	2.064328	2.859611
H	−0.421514	1.235769	4.448095
H	1.175270	1.681557	3.844558
O	−1.068111	−2.907475	−0.736985
Fe ₂ (MoO ₄) ₃ +MeGO			
Mo	−2.505502	2.150071	−1.076351
Fe	0.105110	1.594088	0.505421
O	−1.876449	2.104635	−2.674193
O	−1.202983	2.722056	0.211959
O	−3.856631	3.195237	−1.048812
O	−3.026364	0.366702	−0.499084
Mo	2.234579	2.306322	−1.850441
O	1.554782	3.675501	−2.625361
O	3.940309	2.455163	−1.907009
O	1.651978	2.199025	−0.017957
O	1.623796	0.696348	−2.638788
Mo	0.508790	−0.874412	−2.446093
O	0.235584	−1.303587	−4.077150
O	−0.310877	0.319666	−0.710042
O	−1.315792	−1.591896	−1.784355
O	1.547248	−2.070296	−1.798570
Fe	−1.736250	−0.778755	−0.379326
C	0.303623	−0.365442	2.400757
C	−0.337467	−1.524920	1.976969
C	0.120000	−2.880584	2.428510
O	−0.102118	0.855752	2.113338
O	−1.412281	−1.524711	1.205301
H	1.165718	−0.444338	3.063839
H	0.466134	−3.458059	1.563350
H	0.930289	−2.811619	3.156934
H	−0.720226	−3.424950	2.871157
Fe ₂ (MoO ₄) ₃ +O+MeGO			
Mo	−2.299561	1.742462	0.027715
Fe	0.777277	1.418993	0.031975
O	−2.357121	1.781316	−1.704371
O	−0.547630	2.385641	0.585375
O	−3.618706	2.591417	0.710010
O	−2.201904	−0.055816	0.539046
Mo	2.170012	2.886474	−1.898632
O	2.077673	4.594187	−1.882250
O	3.382177	2.432799	−3.012665
O	2.383738	2.123578	−0.124444
O	0.478664	1.974394	−1.977583
Mo	−0.330070	0.260509	−2.890606
O	−1.140454	0.853178	−4.271781
O	0.351055	−0.121600	−0.645589
O	−1.462260	−1.062783	−2.105170

O	1.054594	−0.531495	−3.511762
Fe	−1.092342	−1.202935	−0.346188
C	0.796386	0.271905	2.826216
C	−0.680162	0.360404	3.259458
C	−1.370986	−0.932010	3.588695
O	1.295360	0.696142	1.788677
O	−1.130595	1.478466	3.404814
H	1.491632	−0.173144	3.559824
H	−2.429346	−0.739693	3.770580
H	−1.255382	−1.664488	2.783496
H	−0.918858	−1.360478	4.493256
O	−0.942191	−2.605423	0.308904
Fe ₂ (MoO ₄) ₃ +HA			
Mo	−2.309050	1.034389	−0.865463
Fe	0.718926	1.113256	−0.348855
O	−1.887107	1.122086	−2.570022
O	−0.866013	1.833630	0.093566
O	−3.825947	1.755560	−0.519351
O	−2.233691	−0.738453	−0.320779
Mo	2.508437	2.493300	−1.857949
O	2.525055	4.208441	−1.901914
O	3.879563	1.922873	−2.710099
O	2.357343	1.802753	−0.055050
O	0.802491	1.715724	−2.292156
Mo	0.060422	−0.072116	−3.381025
O	−0.529804	0.357604	−4.926364
O	0.424702	−0.379608	−1.085833
O	−0.884604	−1.594027	−2.739488
O	1.653562	−0.641133	−3.698054
Fe	−0.739225	−1.691138	−0.891074
C	−0.158050	−0.216860	2.319127
C	−0.455102	−1.709402	2.127091
C	−0.715626	−2.507097	3.370391
O	0.906602	0.219905	1.453401
O	−0.512559	−2.246699	1.018687
H	0.119207	−0.025754	3.358305
H	−1.065207	0.353455	2.090681
H	−1.074560	−3.505356	3.119601
H	0.208110	−2.581342	3.958134
H	−1.449872	−1.990802	4.000691
H	1.605996	0.691812	1.940806
Fe ₂ (MoO ₄) ₃ +O+HA			
Mo	−2.322984	1.757731	−0.665690
Fe	0.751707	0.893892	−0.326943
O	−2.396980	2.106582	−2.351803
O	−0.512437	2.044724	−0.014704
O	−3.484948	2.718157	0.146430
O	−2.567365	−0.087026	−0.387434
Mo	2.211360	2.095977	−2.410143
O	2.039842	3.788208	−2.579278
O	3.451805	1.576870	−3.466087
O	2.441461	1.551438	−0.609660
O	0.547832	1.040647	−2.429801
Mo	0.086106	−0.609751	−3.462638
O	−0.127693	−0.320465	−5.132736
O	0.055532	−0.660741	−0.254499
O	−1.461237	−1.289322	−2.680750

O	1.391653	−1.710261	−3.284762
Fe	−1.444746	−1.389108	−0.878464
C	1.136455	−0.405570	2.361035
C	−0.328406	−0.571264	2.781281
C	−0.678766	−1.927993	3.349305
O	1.296838	0.796676	1.568104
O	−1.125117	0.334337	2.650442
H	1.480931	−1.281225	1.802997
H	1.747570	−0.289796	3.263611
H	−1.586762	−1.850586	3.949354
H	−0.869360	−2.615171	2.515555
H	0.135946	−2.350409	3.947715
O	−1.742344	−2.767489	−0.223496
H	2.232105	1.078937	1.563059
Fe ₂ (MoO ₄) ₃ +FD			
Mo	−2.051516	0.640811	1.303324
Fe	0.997665	0.220121	1.291314
O	−1.915149	0.946690	−0.423259
O	−0.406023	1.131358	2.042645
O	−3.336835	1.530576	1.996128
O	−2.284599	−1.251164	1.479486
Mo	2.766397	1.630498	−0.278140
O	3.023172	3.316531	−0.097270
O	3.926989	1.018592	−1.378758
O	2.750393	0.710699	1.401267
O	0.914856	1.121014	−0.569020
Mo	−0.189459	−0.214771	−1.754202
O	−0.881983	0.637323	−3.057636
O	0.208598	−1.061172	0.427741
O	−1.355492	−1.747465	−1.320438
O	1.160240	−1.003176	−2.455506
Fe	−1.186293	−2.103438	0.382132
C	1.783905	−0.337020	3.932494
O	1.180624	−0.787157	2.961767
H	2.254034	0.654055	3.907065
H	1.853476	−0.951906	4.839866

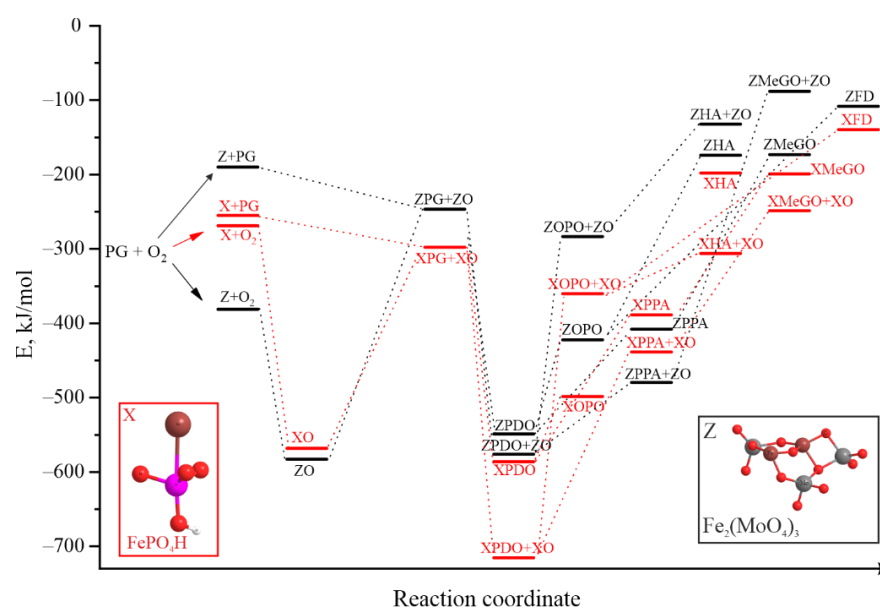


Figure S4. Interactions of key reagents, intermediates and products with active sites along the reaction coordinate (B3LYP/DGDZVP level of theory).