Electronic supplementary information (ESI)

Design of a catalyst through Fe doping boron cage $B_{10}H_{14}$ for CO_2 hydrogenation and investigation of the catalysis character of iron hydride (Fe-H)

Lei Qian,[a] Kai-Yang Ma,[a] Zhong-Jun Zhou[b] and Fang Ma*[a]

[a] School of Chemistry and Materials Science, Huaibei Normal University, Huaibei, 235000, China.
E-mail: mafangchem@foxmail.com.
[b] Institute of Theoretical Chemistry, Jilin University, Changchun,130023, China.

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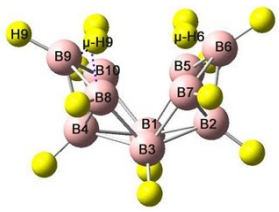
Table S1. Comparisons of geometrical parameters (Å) of $B_{10}H_{14}$ at different theory level and experimental data.

bond	$B_{10}H_{14}$(exptl)[a]	$B_{10}H_{14}$[b]	$B_{10}H_{14}$[c]	$B_{10}H_{14}$[d]	$B_{10}H_{14}$[e]
B_2-B_5	1.74±0.03	1.789	1.785	1.792	1.791
B_5-B_6	1.76±0.03	1.786	1.780	1.790	1.790
B_5-B_1	1.74±0.02	1.749	1.749	1.750	1.749
B_2-B_1	1.79±0.04	1.781	1.778	1.785	1.785
B_6-B_2	1.73±0.04	1.724	1.722	1.723	1.724
B_6-B_7	1.78±0.03	1.786	1.780	1.790	1.790
B_7-B_3	1.74±0.02	1.749	1.749	1.750	1.749
B_1-B_3	1.78±0.02	1.776	1.774	1.784	1.784
B_9-B_6		3.592	3.582	3.595	3.595
B_7-B_5		2.837	2.829	2.845	2.845
B_7-B_8	2.01±0.02	1.989	1.988	1.991	1.991
B_9-μ-H_9	1.40±0.05	1.333	1.333	1.335	1.335
B_8-μ-H_9	1.34±0.05	1.322	1.319	1.318	1.318
B_9-H_9	1.25±0.05	1.190	1.188	1.181	1.181

$B_{10}H_{14}$



[a] For experimental data see ref: Gaines, D. F. *Inorg. Chem.* **2000**, *39*, 1812–1813. [b] At the CCSD/6-31+G* level of theory. [c]At the MP2/6-31+G* level of theory. [d] At the B3LYP/6-311+G(d,p) level of theory in this work. [e]At the B3LYP/6-311G(d,p) level of theory.

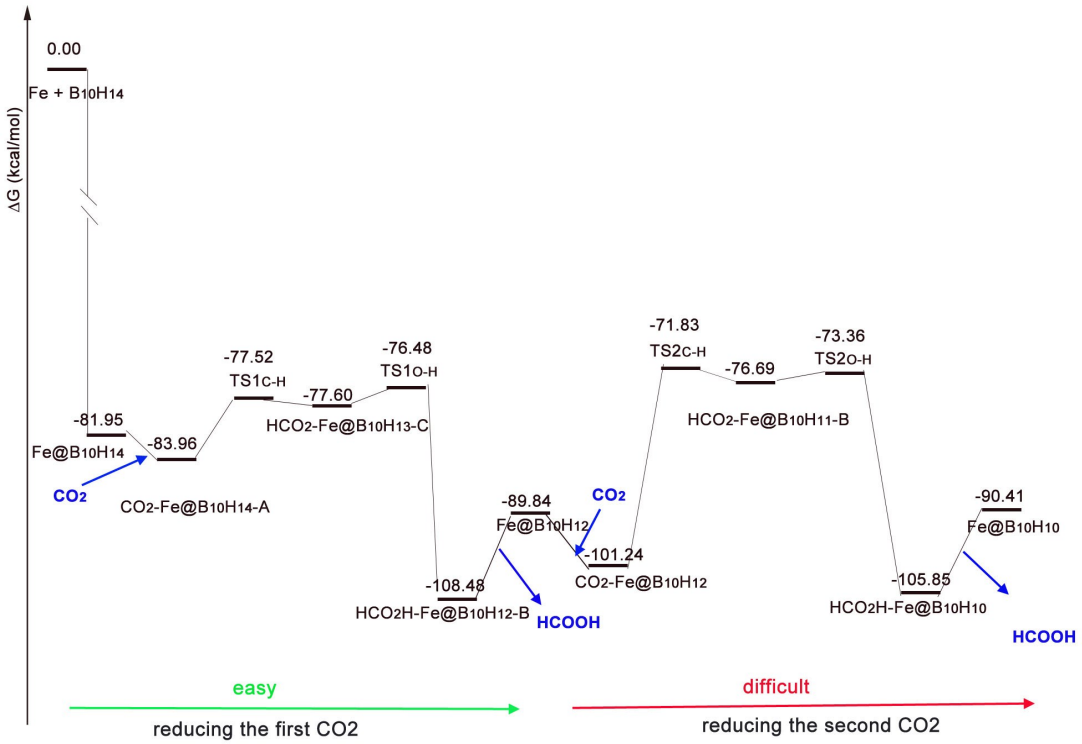


Fig S1. The whole free energy profile for an equivalent of $Fe@B_{10}H_{14}$ reducing double CO_2 at the M06 level.

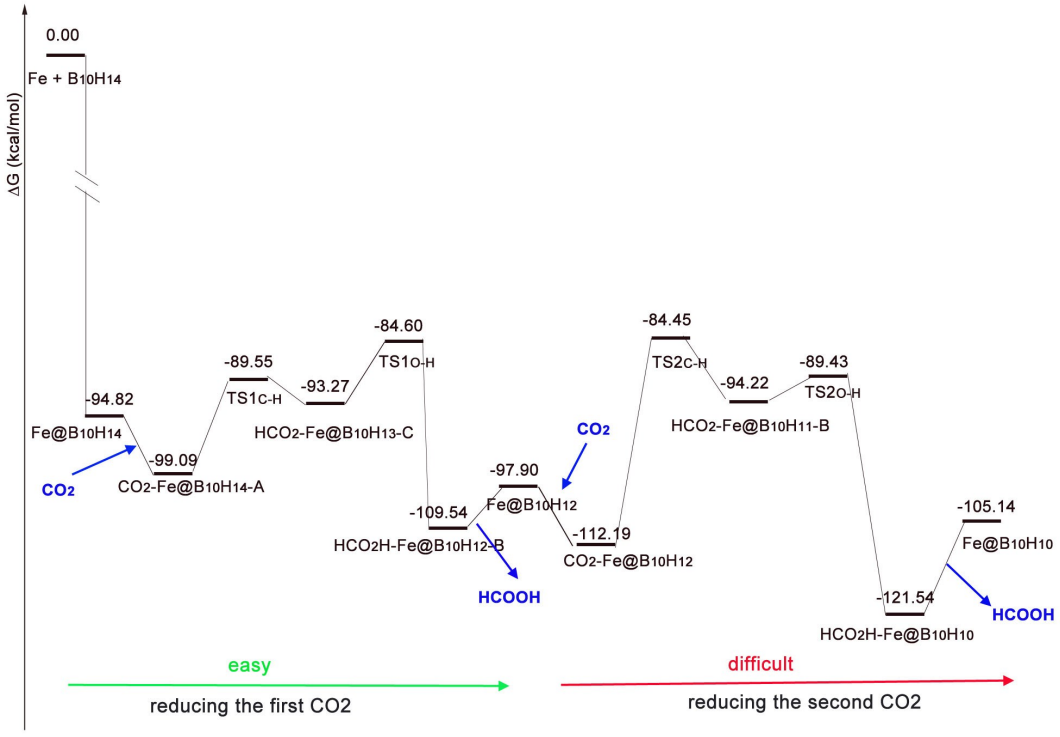


Fig S2. The whole free energy profile for an equivalent of $Fe@B_{10}H_{14}$ reducing double CO_2 at the MP2 level.

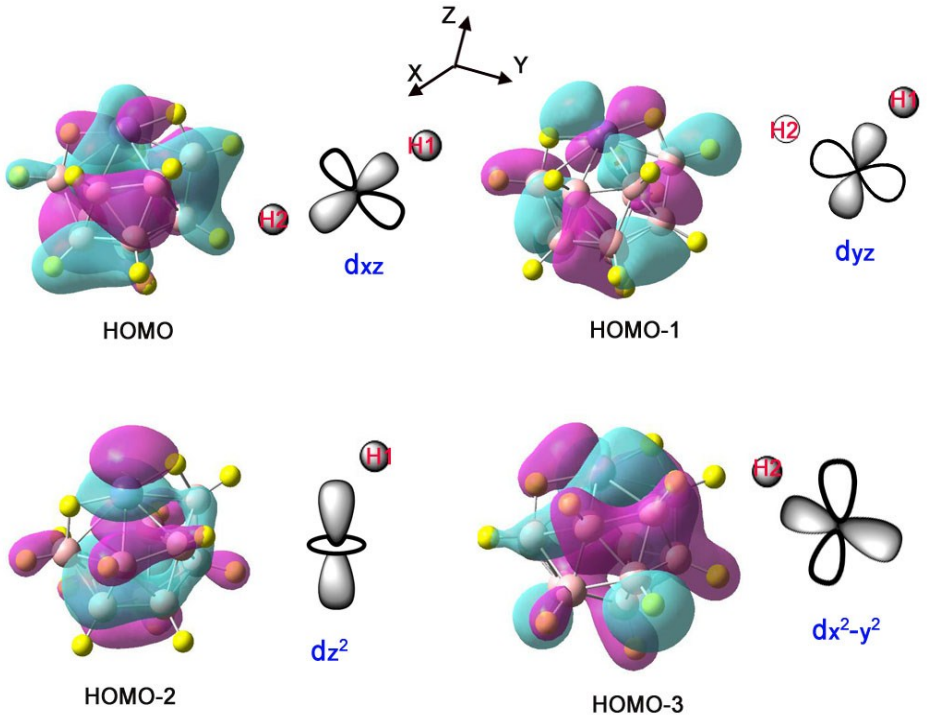


Fig S3. Different interaction modes between Fe atom with H1 and H2 atoms.

Atomic coordinates of intermediates and key transition states

$TS1_{C-H}$

5	-2.839171	0.103640	-0.282047
5	-2.167462	-1.495310	0.172936
5	-2.219594	-0.167457	1.360701
5	-2.022763	1.424266	0.598671
5	-1.826598	-0.733075	-1.436089
5	-0.734884	-1.095461	1.205119
5	-0.639724	0.641249	1.384494
5	-1.878177	1.240430	-1.184750
1	-3.977001	0.186145	-0.601427
1	-2.853256	-2.452635	0.286368
1	-2.910920	-0.241241	2.317036
1	-2.597364	2.356896	1.045947
1	-2.080247	-1.106537	-2.529362
1	-0.313010	-1.829139	2.034436
1	-0.047905	1.119370	2.290623
1	-2.390861	1.922921	-2.002605
5	-0.474524	1.804398	-0.133875
5	-0.590440	-1.614926	-0.445085
1	-0.151720	2.948124	-0.118328
1	0.750973	1.372460	-0.010114
1	-0.610068	1.461141	-1.424615
1	-0.477515	-0.708727	-1.465826
1	1.803223	-0.188025	1.041959
1	0.230980	-2.439808	-0.747285
26	0.838562	-0.200271	-0.141623
6	3.102547	0.086935	0.012140
8	2.571242	0.052478	-1.086036
8	4.021363	0.199637	0.721695

$TS1_{O-H}$

5	1.557703	0.756380	1.450850
5	1.927609	-0.963012	1.257811
5	2.702459	0.236360	0.201065
5	1.696966	1.693336	-0.095320
5	0.221864	-0.384704	1.328707
5	2.240672	-1.318695	-0.448120
5	1.957034	0.460551	-1.371082
5	0.076549	1.291542	0.604280
1	1.859420	1.316931	2.446635
1	2.496969	-1.529100	2.126935
1	3.876493	0.402381	0.188960

1	2.180044	2.772164	-0.081552
1	-0.542752	-0.652697	2.193635
1	3.043890	-2.041781	-0.928238
1	2.437964	0.493460	-2.451323
1	-0.521890	2.177558	1.131411
5	0.409189	1.394038	-1.147149
5	0.660903	-1.743396	0.327365
1	-0.169718	2.060862	-1.937916
1	0.628843	0.183127	-1.735458
1	-1.320445	0.992080	0.304569
1	-4.233390	-0.415063	0.436149
1	1.121244	-1.801187	-0.919123
1	0.156169	-2.807853	0.475938
6	-3.204147	-0.067461	0.290876
8	-2.396221	-0.921494	-0.242627
8	-2.861824	1.071466	0.617164
26	-0.673783	-0.358691	-0.639971

$TS2_{C\text{-}H}$

5	2.103888	0.414866	1.260622
5	2.010252	-1.281109	0.721473
5	2.634410	-0.004476	-0.365176
5	1.930708	1.590379	-0.082845
5	0.552269	-0.449658	1.480764
5	1.506786	-1.209421	-1.010390
5	1.295183	0.519984	-1.430632
5	0.535587	1.214219	1.030450
1	2.797151	0.711904	2.172361
1	2.700728	-2.094384	1.234603
1	3.742918	-0.067029	-0.775082
1	2.604448	2.562462	-0.134365
1	0.005398	-0.735252	2.496231
1	1.736445	-1.983908	-1.877149
1	1.252370	0.738993	-2.602492
1	-0.100221	1.949533	1.712201
5	0.317147	1.716251	-0.656438
5	0.410285	-1.780109	0.361372
1	-0.271168	2.649221	-1.077782
1	-1.532036	1.038078	0.055741
1	0.122098	-1.516210	-0.959229
1	-0.135454	-2.809258	0.549142
26	-0.567105	-0.077085	-0.400876
6	-2.787084	0.045550	0.153716
8	-2.345755	-0.998435	-0.301656

8	-3.649372	0.693449	0.607585

$TS2_{O-H}$

5	1.877191	0.972382	1.107290
5	2.244930	-0.768049	0.973859
5	2.608352	0.349394	-0.375086
5	1.444307	1.700571	-0.473048
5	0.597258	-0.179844	1.577691
5	1.750884	-1.157617	-0.739002
5	1.239576	0.246651	-1.542919
5	0.173160	1.339529	0.762547
1	2.402565	1.629739	1.939665
1	3.088955	-1.278598	1.630842
1	3.731330	0.539198	-0.694174
1	1.799840	2.782795	-0.799419
1	0.050283	-0.376646	2.612262
1	2.054594	-2.104270	-1.389882
1	1.236460	0.218305	-2.731427
1	-0.494005	2.100698	1.379293
5	-0.115379	1.235667	-1.010520
5	0.816534	-1.621242	0.641227
1	-0.905181	1.760155	-1.718502
1	-1.214652	0.974384	0.135114
1	-4.163257	-0.260268	0.264693
1	0.169319	-2.625107	0.702943
26	-0.460926	-0.619401	-0.339936
6	-3.108037	0.023177	0.179156
8	-2.300507	-0.923777	-0.170165
8	-2.737994	1.175998	0.397888

$TS_{H-adsorb}$

5	-1.757850	0.265788	1.008711
5	-1.115167	1.600655	0.010235
5	-1.794632	0.142802	-0.767498
5	-1.556186	-1.338099	0.222846
5	-0.129121	0.937489	1.390771
5	-0.184948	0.750790	-1.305217
5	-0.472635	-0.945853	-1.215167
5	-0.415423	-0.754583	1.547244
1	-2.700144	0.473802	1.695502
1	-1.675065	2.644448	-0.050449
1	-2.765023	0.256897	-1.436969
1	-2.377497	-2.189346	0.298800
1	0.278401	1.469553	2.375545
1	0.180123	1.140953	-2.369852

1	-0.271300	-1.575191	-2.203335
1	-0.171735	-1.242357	2.603545
5	0.095560	-1.704716	0.214067
5	0.593170	1.646994	-0.028352
1	1.116477	-2.363232	0.238402
1	1.338212	2.564648	-0.107332
26	1.205998	-0.234863	0.089226
1	3.082954	0.257277	0.016041
1	2.720044	0.939390	-0.023053
$TS2_{H-H}$			
5	1.677963	-0.003913	1.018174
5	1.258104	-1.486339	0.122645
5	1.809523	-0.006295	-0.735858
5	1.293189	1.475087	0.075438
5	0.158908	-0.831926	1.386901
5	0.453680	-0.917145	-1.406947
5	0.374985	0.861241	-1.366831
5	0.181230	0.883553	1.359381
1	2.591474	0.016056	1.769443
1	1.937261	-2.450757	0.217642
1	2.819084	-0.044464	-1.349942
1	1.998159	2.423926	0.124248
1	-0.209706	-1.355123	2.386369
1	0.471535	-1.510798	-2.434141
1	0.220381	1.420707	-2.406216
1	-0.236574	1.444909	2.317513
5	-0.398994	1.892923	-0.104915
5	-0.476212	-1.860965	0.051917
1	-0.643530	3.052418	-0.146316
1	-1.650474	1.494842	0.222062
1	-0.876367	-1.147433	-1.196210
1	-0.807202	-2.992522	-0.027434
26	-1.270017	0.029789	-0.105570
1	-1.815281	-1.299473	0.446008
1	-2.440198	0.142092	0.822257