Electronic Supplementary Materials

Bioinspired Design and Computational Prediction of SCS Nickel Pincer Complexes for Hydrogenation of Carbon Dioxide

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1. Evaluation of density functionals

In order to examine the reliability of density functionals for this Ni system, we also calculated the relative free energies between **4** and **TS**$_{1,2}$ using eight other widely used functionals with different Hartree-Fock exchanges, including pure density functionals TPSS [1], M06L [2], PBE [3] and hybrid density functionals B3LYP [4,5], B3PW91 [6], PBE0 [3], TPSSh [1], and HSE06 [7]. All structures were independently optimized using above eight functionals with the same basis set described in Computation Details. The calculated absolute and relative free energies are listed in Table S1.

We can see that the pure density functionals without Hartree-Fock exchanges have slightly lower relative free energies. The largest difference of 7.4 kcal/mol are the relative energies obtained by using the PBE and B3LYP functionals. Such difference indicates that the Hartree-Fock exchange has a moderate influence to this nickel catalytic system. The M06 result of 23.2 kcal/mol is in the middle of them, and close to the results of TPSS, M06L, PBE, B3PW91, TPSSh and HSE06 functionals. Therefore, we believe M06 is a suitable functional for the DFT study of this Ni system.

Table S1. Absolute and relative free energies of rate-determining states **4** and **TS**$_{1,2}$ calculated by using different density functionals.

Functionals	Absolute free energies (Hartree)		Relative energies (kcal/mol)
	4	**TS**$_{1,2}$	**4** → **TS**$_{1,2}$
M06	−1651.005941	−1650.969177	23.1

TPSS	−1651.560480	−1651.524512	22.7
M06L	−1651.403417	−1651.369426	21.4
PBE	−1650.347971	−1650.314786	20.8
B3LYP	−1651.482168	−1651.437295	28.2
B3PW91	−1651.147957	−1651.106173	26.3
PBE0	−1650.333634	−1650.289141	27.9
TPSSh	−1651.432370	−1651.392831	24.8
HSE06	−1650.421030	−1650.378566	26.6

2. Electronic energies of singlet and triplet states

In order to find out the correct spin states of the SCS nickel complexes in this study, we also calculated the triplet state energies of all intermediates. The absolute and relative electronic energies of the singlet and triplet states of those intermediates are listed in Table S2. The triplet state energies were obtained by optimizing the intermediate structures as triplets except a few triplet states cannot converge. We can see although intermediates **3**, **5**, and **10**'s triplet states are only a few kcal/mol higher than their singlet states, the triplet states of most intermediates are more than 10 kcal/mol higher than the corresponding singlet states. Such results indicate that the CO_2 hydrogenation reaction catalyzed by the proposed SCS nickel complexes undergoes low-spin pathways without spin-crossover.

Table S2. Absolute and relative electronic energies of singlet and triplet states.

Complex	E_S (Hartree)	E_T (Hartree)	$E_T - E_S$ (kcal/mol)
1	−1462.602668	−1462.564174	24.2
2 [a]	−1651.116831	−1651.073257	27.3
3	−1461.860351	−1461.858009	1.5
4	−1651.146786	−1651.123080	14.9
5	−1651.141771	−1651.115496	16.5
6	−1461.430973	−1461.423755	4.5

7	−1462.621357	−1462.589609	19.9
8 [a]	−1652.285066	−1652.254482	19.2
8'	−1652.315309	−1652.299651	9.8
9	−1652.343745	−1652.316364	17.2
10	−1652.298383	−1652.287594	6.8
11	−1537.845386	−1537.823719	13.6
12	−1537.873176	−1537.844480	18.0
13	−1651.861892	−1651.832547	18.4
14	−1537.402105	−1537.368525	21.1
15 [a]	−1577.063111	−1577.013807	30.9
15' [a]	−1577.099795	−1577.045953	33.8
16	−1577.133932	−1577.104348	18.6

[a] The geometric optimizations for triplet states cannot converge. The triplet states energies are obtained from single point calculations using the optimized singlet state structures.

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