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Supplementary information

Computational prediction of pentadentate iron and cobalt complexes as a mimic of mono-iron hydrogenase for hydrogenation of carbon dioxide to methanol

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1. Computational details

All DFT calculations were performed using the Gaussian 09 suite of programs[1] for a hybrid meta-GGA level M06 functional[2] in conjugation with all-electron 6-31++G(d,p) basis set[3-5]. An ultrafine grid (99,590) was used for numerical integrations. All structures were fully optimized in water (ε = 78.36) using the integral equation formalism polarizable continuum model (IEFPCM)[6] with SMD radii[7] for solvent effect corrections. Thermal corrections were calculated within the harmonic potential approximation on optimized structures under 298.15 K and 1 atm pressure. Unless otherwise noted, the relative energies reported in the text are Gibbs free energies with the solvent effect corrections. The optimized structures were confirmed to have no imaginary vibrational mode for all equilibrium structures and only one imaginary vibrational mode for each transition state. Transition states were further characterized by intrinsic reaction coordinate (IRC) calculations to affirm that the stationary points were correctly connected. The 3D molecular structures were drawn by using the JIMP2 molecular visualizing and manipulating program.[8]

2. Evaluation of density functionals

In order to evaluate the dependence of density functionals of the proposed cobalt catalytic system, we calculated the relative free energies between intermediate **IS-1a$_{\mathbf{Co}}$** and transition state **TS-1a$_{\mathbf{Co}}$** using other seven widely-used and/or recently developed functionals, including pure functionals PBE[9,10] and TPSS,[11] and hybrid functionals B3LYP,[12,13] B3PW91,[14,15] PBE0,[16,17] ωB97X-D[18], and TPSSh,[11,19] with the same all-electron 6-31++G(d,p) basis set. As shown in Table S1, the M06 functional has the highest relative energy of 21.8 kcal/mol, which indicates that our calculations results will not underestimate the energy barriers of the reaction catalyzed by **1a$_{\mathbf{Co}}$**. In addition, the M06 result of 21.8 kcal/mol is very close to the results of PBE0, TPSSh, *ω*B97X-D, PBE, B3LYP, and TPSS functionals. Therefore, we believe the M06 functional is suitable for the computational study of this cobalt based catalytic system.

Table S1. Absolute and relative free energies of **IS-1a$_{\mathbf{Co}}$** and **TS-1a$_{\mathbf{Co}}$** calculated by using different density functionals.

Functionals	Absolute free energies (Hartree)		Total barriers (kcal/mol)
	IS-1a$_{\mathbf{Co}}$	**TS-1a$_{\mathbf{Co}}$**	**IS-1a$_{\mathbf{Co}}$** → **TS-1a$_{\mathbf{Co}}$**
PBE	−2894.648975	−2894.618495	19.1
TPSS	−2896.928933	−2896.898808	18.9
B3LYP	−2896.597620	−2896.567194	19.1
B3PW91	−2895.972418	−2895.946766	16.1
PBE0	−2894.656885	−2894.622814	21.4
*ω*B97X-D	−2896.121134	−2896.089865	19.6
TPSSh	−2896.704181	−2896.672336	20.0
M06	−2895.559527	−2895.524714	21.8

3. Spin state evaluation

Table S2. Absolute and relative free energies of singlet and triplet states of key structures in the reaction catalysed by **1a$_{\mathbf{Co}}$**.

Structures	Absolute free energies (Hartree)		Relative energies (kcal/mol)
	Singlet	Triplet	
1a$_{\mathbf{Co}}$	−2703.520547	−2703.517163	2.1
2a$_{\mathbf{Co}}$	−2704.685332	−2704.677916	4.7
3a$_{\mathbf{Co}}$	−2704.709562	−2704.686420	14.5
4a$_{\mathbf{Co}}$′	−2893.222653	−2893.196265	16.6
7a$_{\mathbf{Co}}$	−2894.383951	−2894.363322	12.9
8a$_{\mathbf{Co}}$	−2894.380241	−2894.352294	17.5
9a$_{\mathbf{Co}}$	−2779.939367	−2779.916034	14.6
10a$_{\mathbf{Co}}$	−2779.946787	−2779.921129	16.1

In order to find out the correct spin multiplicities of the ground states in the reaction catalysed by **1a$_{\mathbf{Co}}$**, we optimized the triplet state structures of key structures in the reaction pathway, **1a$_{\mathbf{Co}}$**, **2a$_{\mathbf{Co}}$**, **3a$_{\mathbf{Co}}$**, **4a$_{\mathbf{Co}}$′**, **7a$_{\mathbf{Co}}$**, **8a$_{\mathbf{Co}}$**, **9a$_{\mathbf{Co}}$**, and **10a$_{\mathbf{Co}}$**, and listed the absolute and relative free energies of their singlet and triplet states in Table S2. We can see that although the free energies of the singlet and triplet states of **1a$_{\mathbf{Co}}$** and **2a$_{\mathbf{Co}}$** are close, their triplet states are still still 2.1 and 4.7 kcal/mol higher than their singlet states, respectively. All other triplet states are significantly higher than the corresponding singlet states. Therefore, we believe reaction catalyzed by **1a$_{\mathrm{Co}}$** goes through a low-spin pathway.

4. Evaluation of catalyst 1b$_{\mathrm{Co}}$

The free energy difference between **TS-1b$_{\mathrm{Co}}$** and **IS-1b$_{\mathrm{Co}}$** is only 0.6 kcal/mol higher than the difference between **TS-1a$_{\mathrm{Co}}$** and **IS-1a$_{\mathrm{Co}}$**. In order to evaluate catalytic activity of **1b$_{\mathrm{Co}}$**, we further calculated key transition states in the reaction catalyzed by **1b$_{\mathrm{Co}}$**, including the transition state for the formation of HCOOH molecule (**TS1-1b$_{\mathrm{Co}}$**) and the transition state for the formation of CH_2O molecule through C−O bond cleavage (**TS2-1b$_{\mathrm{Co}}$**). Table S3 shows the absolute and relative free energies of **IS-1b$_{\mathrm{Co}}$**, **TS-1b$_{\mathrm{Co}}$**, **TS1-1b$_{\mathrm{Co}}$**, and **TS1-1b$_{\mathrm{Co}}$**. We found that the free energy difference between **TS2-1b$_{\mathrm{Co}}$** and **IS-1b$_{\mathrm{Co}}$** is 26.0 kcal/mol, which is already 2.7 kcal/mol higher than the total free energy barrier of **1a$_{\mathrm{Co}}$**. Therefore, we believe **1a$_{\mathrm{Co}}$** is a more promising catalyst candidate for the reaction.

Table S3. Absolute and relative free energies of **IS-1b$_{\mathrm{Co}}$**, **TS-1b$_{\mathrm{Co}}$**, **TS1-1b$_{\mathrm{Co}}$**, and **TS1-1b$_{\mathrm{Co}}$** in the reaction catalysed by **1b$_{\mathrm{Co}}$**.

Structures	Absolute free energies (Hartree)	Relative energies of **IS** → **TS** (kcal/mol)
IS-1b$_{\mathrm{Co}}$	−2932.509357	——
TS-1b$_{\mathrm{Co}}$	−2932.473430	22.5
TS1-1b$_{\mathrm{Co}}$	−2932.474540	21.8
TS2-1b$_{\mathrm{Co}}$	−2932.467981	26.0

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