Theoretical DFT Study on the Mechanisms of CO/CO₂ Conversion in Chemical Looping Catalyzed by Calcium Ferrite

Jing Wang, Jiande Gu,* Asif Rony, Maohong Fan, and Jerzy Leszczynski*

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ABSTRACT: The CO/CO₂ conversion mechanism on the calcium ferrite (CFO) surface in chemical looping was explored by a computational study using the density functional theory approach. The CFO catalytic reaction pathway of 2CO + O₂ → 2CO₂ conversion has been elucidated. Our results show that the Fe center in CFO plays the key role as a catalyst in the CO/CO₂ conversion. Two energetically stable spin states of CFO, quintet and septet, serve as the effective catalysts. The presence of the triplet O₂ molecule caused the conversion of these two spin-state structures into each other along the catalytic reaction pathway. A double release of CO₂ was predicted following this reaction mechanism. The rate-determining step is the formation of the 2CO₂−CFO complex (P4) in the quintet state (19.0 kcal/mol). The predicted energy barriers for all the steps suggest that the proposed pathway is plausible.

1. INTRODUCTION

Chemical looping combustion (CLC) technology is a unique approach that uses oxygen carriers (OCs) to supply oxygen to fossil fuels that may be used in coal utilization. This process could also generate clean energy with lowering carbon emissions. It is broadly applied for carbon dioxide capture, emission reduction, and energy conservation.¹⁻³ Chemical looping to lower CO₂ emissions is an important technological approach in the production of energy and chemicals. The selection and development of suitable OC materials for chemical looping rely on their reactivity, cost, toxicity, thermal stability, attrition resistance, and chemical stability.⁴ The chemical looping for oxidative coupling of methane was studied with a Mn⁻⁻⁻Mg-based catalytic OC which showed stable performance in a fixed bed for 100 cycles for more than 50 h.⁵ Various catalysts have been used for the oxidation of carbon monoxide to carbon dioxide. Quasicubic α-Fe₂O₃ nanoparticles were synthesized by a simple solvothermal method and exhibited excellent catalytic activity in the oxidation of CO.⁶ Iron oxide clusters (FeO₁⁻⁻³ and Fe₂O₄) were used for carbon monoxide (CO) oxidation by O₂ in a fast flow reactor. For investigation of the details of experimentally studied reactions, quantum chemical methods were used. Density functional theory (DFT) was applied to further augment the experimental observations with detailed reaction mechanisms. The reaction pathways included two steps: carbon—iron interaction to form the initial intermediate and Fe—O bond activation. Three model catalytic cycles were explored for the CO oxidation by O₂ over iron oxide clusters of FeO₁⁻⁻³, Fe₂O₅, and Fe₂O₄. All the rate-determined steps were found to involve the O—O activation.⁷ The mechanisms of iron-based catalysts Fe₂O₁⁻⁻³ applied toward CO and CH₄ conversion were explored through DFT calculations. The results suggested that Fe—O bond activation is the rate-determined step for the oxidation of CO. For the oxidation of CH₄ by Fe₂O₅, the dissociation of CH₄ governed the process.⁸ Another type of catalyst is based on M₁/γ-Al₂O₃ structures. Geometries, stabilities, and CO oxidation catalytic activities of M₁/γ-Al₂O₃ (M = Pd, Fe, Co, and Ni) were studied through the DFT approach using a slab model. The Ni₁/Al₂O₃ catalyst reveals higher activity in CO oxidation than Pd₁/Al₂O₃.⁹ Interestingly, the CO oxidation processed through the Mars—van Krevelen mechanism whose rate-determining step is the formation of CO₂ from CO through the abstraction of surface oxygen.⁹ Ca₂Fe₂O₅ was found to be a promising OC for CO/CH₄ conversion and H₂ production with a two-step chemical looping hydrogen generation process in the fuel reactor, steam reactor, and air reactor.¹⁰ An inner-looping redox reaction and promoting mechanisms are proposed for the H₂-rich gas production with tar abatement over the bifunctional Ca₂Fe₂O₅ catalyst.¹¹ DFT studies on the reaction
between hematite and methane during chemical looping suggested that dissociations of CH$_4$ are the rate-determining step, while production and dissociation of H$_2$O are reversible. In the chemical looping process, the formation of CO is more favored than that of CO$_2$.

Nanoparticles of Fe$_2$O$_3$ were found to be much more effective as carbon monoxide catalysts than the non-nano-oxide powder. When compared to its oxide parents, N-doped Ca$_3$Fe$_2$O$_5$ brownmillerite enhanced the catalysis activity and electrical conductivity. This will help to design stable and cost-effective oxygen reduction reaction catalysts.

Solid CaO modified by the Fe$_2$O$_3$ OC was used in CLC cycling experiment in oxidation and reduction cycles. It shows better performances in reduction and oxidation than unmodified Fe$_2$O$_3$. It is considered to be a potentially viable material as an OC to produce hydrogen. Interestingly, p-type Ca$_3$Fe$_2$O$_5$ was applied as a photocathode in a water-splitting photo-electrochemical cell. Brownmillerite-type calcium ferrite (Ca$_3$Fe$_2$O$_5$) was prepared for propylene (C$_3$H$_6$) combustion as a catalyst for the formation of oxygen adspecies (O$_2^-$) in the surface layer.

Based upon the experimental observations, DFT was employed to investigate the mechanisms of CO/CO$_2$ conversions when O$_2$ was brought into the chemical looping process. The conversions occurred on the surface of calcium ferrite (CFO) around the Fe site, where the CFO acts as the catalyst in the CO/CO$_2$ conversions. Regarding all the possible spin multiplicity of iron considered, a plausible cyclic catalyst pathway was proposed using the computational approach.

2. METHOD OF COMPUTATIONS

The DFT method along with the functional by Peverati and Truhlar (MN12-L) has been adopted in the present study. The localized basis set, namely, the split valence basis set SVP of Ahlrichs and co-workers, was applied. Previous studies demonstrated that reasonable estimations of the Fe–Al–O interactions were achieved by the MN12-L functional (with double and triple $\zeta$ basis sets, i.e., SV and TZV). All the studied models have been fully optimized by analytical gradient techniques. In the analysis of harmonic vibrational frequencies, the force constants were determined analytically for all the compounds both in the local minima and in the transition state structures on the potential energy surface (PES). The stationary structures were verified by all positive harmonic frequencies. The corresponding transition state structures (TS) were proved by the existence of single imaginary vibrational frequencies as the saddle points on the corresponding PES. An intrinsic reaction coordinate analysis was performed to confirm that a TS is the saddle point that connects the corresponding minima. All the calculations were carried out by the Gaussian 16 package of programs. All the energies discussed below are zero-point-corrected.

3. RESULTS AND DISCUSSION

3.1. Structure of CFO (Ca$_3$Fe$_2$O$_5$).

The structure of Ca$_3$Fe$_2$O$_5$ brownmillerite in the present study was adopted from its crystal structure.

A model of CFO was built as shown in Figure 1. Fe$^{3+}$ may adopt different electron configurations depending on its point group and spin state. Spin multiplicity of Fe$^{3+}$ may reveal as the doublet (with 2S + 1 = 2), quartet, and sextet. The spin multiplicity of model CFO (with two Fe$^{3+}$) may therefore be assumed to range from singlet, triplet, quintet, septet and nonet. All the abovementioned spin states for model CFO were examined. The quintet spin model has been found to represent the most stable structure, which has slightly lower in energy (by 1.40, 1.33, and 0.99 kcal/mol) than that of the singlet, triplet, and septet, respectively, while the model characterized by the nonet spin state is more than 18 kcal/mol higher in energy than the quintet model and therefore will not be discussed further.

**Figure 1. Model CFO used in the study.**

**Figure 2.** Frontier MOs for the quintet CFO and septet CFO models which are all related to the d orbitals of Fe3 and Fe4.
Table 1. Mulliken Charge (in e) and Spin Density of Model CFO with Various Spin Multiplicities

<table>
<thead>
<tr>
<th>CFO</th>
<th>CFO (triplet)</th>
<th>CFO (quintet)</th>
<th>CFO (septet)</th>
<th>CFO (nonet)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca1</td>
<td>1.54</td>
<td>1.53</td>
<td>1.53</td>
<td>1.51</td>
</tr>
<tr>
<td>Ca2</td>
<td>1.53</td>
<td>1.54</td>
<td>1.53</td>
<td>1.51</td>
</tr>
<tr>
<td>Fe3</td>
<td>0.68</td>
<td>0.72</td>
<td>0.75</td>
<td>0.69</td>
</tr>
<tr>
<td>Fe4</td>
<td>0.68</td>
<td>0.72</td>
<td>0.75</td>
<td>0.69</td>
</tr>
<tr>
<td>O5</td>
<td>−0.98</td>
<td>−0.99</td>
<td>−1.02</td>
<td>−0.76</td>
</tr>
<tr>
<td>O6</td>
<td>−0.85</td>
<td>−0.88</td>
<td>−0.88</td>
<td>−0.77</td>
</tr>
<tr>
<td>O7</td>
<td>−0.76</td>
<td>−0.76</td>
<td>−0.77</td>
<td>−0.76</td>
</tr>
<tr>
<td>O8</td>
<td>−0.85</td>
<td>−0.87</td>
<td>−0.87</td>
<td>−0.90</td>
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<tr>
<td>O9</td>
<td>−0.98</td>
<td>−0.99</td>
<td>−0.96</td>
<td>−0.97</td>
</tr>
</tbody>
</table>

Table 2. Geometry Parameters of Model CFO with Various Spin Multiplicities (Atomic Distances in angstrom)

<table>
<thead>
<tr>
<th>CFO (singlet)</th>
<th>CFO (triplet)</th>
<th>CFO (quintet)</th>
<th>CFO (septet)</th>
<th>CFO (nonet)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca1−Ca2</td>
<td>3.149</td>
<td>3.150</td>
<td>3.133</td>
<td>3.143</td>
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<tr>
<td>Fe3−Fe4</td>
<td>2.371</td>
<td>2.368</td>
<td>2.388</td>
<td>2.400</td>
</tr>
<tr>
<td>Fe3−O6</td>
<td>1.810</td>
<td>1.810</td>
<td>1.815</td>
<td>1.792</td>
</tr>
<tr>
<td>Fe3−O8</td>
<td>1.810</td>
<td>1.810</td>
<td>1.862</td>
<td>1.791</td>
</tr>
<tr>
<td>Fe3−O9</td>
<td>1.718</td>
<td>1.717</td>
<td>1.738</td>
<td>1.724</td>
</tr>
<tr>
<td>Fe4−O5</td>
<td>1.718</td>
<td>1.717</td>
<td>1.737</td>
<td>1.780</td>
</tr>
<tr>
<td>Fe4−O6</td>
<td>1.810</td>
<td>1.810</td>
<td>1.835</td>
<td>1.923</td>
</tr>
<tr>
<td>Fe4−O8</td>
<td>1.810</td>
<td>1.810</td>
<td>1.820</td>
<td>1.934</td>
</tr>
<tr>
<td>Ca1−O5</td>
<td>2.345</td>
<td>2.346</td>
<td>2.343</td>
<td>2.345</td>
</tr>
<tr>
<td>Ca1−O7</td>
<td>2.378</td>
<td>2.376</td>
<td>2.371</td>
<td>2.386</td>
</tr>
<tr>
<td>Ca1−O8</td>
<td>2.462</td>
<td>2.461</td>
<td>2.408</td>
<td>2.432</td>
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<tr>
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<td>2.345</td>
<td>2.346</td>
<td>2.343</td>
<td>2.346</td>
</tr>
<tr>
<td>Ca2−O7</td>
<td>2.378</td>
<td>2.377</td>
<td>2.373</td>
<td>2.386</td>
</tr>
<tr>
<td>Ca2−O9</td>
<td>2.345</td>
<td>2.346</td>
<td>2.337</td>
<td>2.351</td>
</tr>
</tbody>
</table>

Scheme 1. CO and CO₂ Conversion Process Cycle by O₂ through the Catalyst CFO

Table 3. Mulliken Charge (in e) and Spin Density of Model CFO with Various Spin Multiplicities

For the ground state (quintet), the population analysis indicates that the spin density on Fe3 amounts to 1.15 with a charge of 0.75 e and that the spin density on Fe4 is 1.96 with a net charge of 0.69 e. Meanwhile, a spin density of 0.98 is located on O7 (with a charge of −0.77 e). Therefore, the four unpaired electrons in the quintet state of the CFO compound are distributed on Fe3(1), Fe4(2), and O7(1), approximately. Accordingly, the molecular orbital (MO) analysis for the quintet state of CFO revealed that the main contributions of d-type orbitals of Fe3 and Fe4 appear in the highest occupied MO (HOMO), HOMO − 1, HOMO − 2, HOMO − 3, HOMO − 4, HOMO − 5, and HOMO − 6 for the α-spin and in the HOMO, HOMO − 1, HOMO − 2, and HOMO − 3 for the β-spin orbitals. Three singly occupied MOs (SMOs) can be recognized as β-spin HOMO − 3, HOMO − 2, and HOMO. On the other hand, the SMO corresponding to the unpaired electron around O7 can be identified in α-spin HOMO − 12 and unoccupied β-spin orbital LUMO (lowest unoccupied MO) + 2 orbitals (corresponding orbitals shown in Figure S1 in the Supporting Information).

For the septet CFO model, the spin density on Fe3 and Fe4 atoms is calculated to be 1.21 with a charge of 0.78 e and 3.57 with a charge of 0.71 e, respectively. Like in the quintet model, the O7 atom is also found to carry a charge of −0.76 e and its spin density is around 1.01. This suggests that the six unpaired electrons of the septet CFO model are allocated on Fe3(1), Fe4(4), and O7(1) atoms. The MO analysis for the septet model demonstrates that the d-type orbitals of Fe3 and Fe4 mostly contribute to the orbitals of HOMO − 7 through the HOMO in the α-spin state and orbitals of HOMO − 2 to the HOMO in the β-spin state.

For the unoccupied α-spin state frontier MOs, d-type orbitals of Fe3 and Fe4 atoms distribute to LUMO + 2, LUMO + 4, LUMO + 5, and LUMO + 6 orbitals and a d-type orbital of Fe3 and Fe4 mixed with the p-type of O6 and O8 atoms dominate the LUMO + 3 orbital. For the β-spin unoccupied orbitals, d-type orbitals of Fe3 and Fe4 contribute to LUMO + 3, LUMO + 5, LUMO + 7, and LUMO + 8 orbitals, LUMO + 4 shows mixed d-type orbitals of Fe3 and Fe4 and s-type orbitals of Fe3, and LUMO + 6 illustrates mixed orbitals of p-type and s-type from both Fe3 and Fe4 (Figure 2).

The Mulliken charges and spin densities of all the atoms at different spin states of the CFO model are listed in Table 1, and the corresponding geometry parameters are displayed in Table 2.

For the singlet CFO structure, the charge distributions on Fe3 and Fe4 atoms are basically the same (0.68 e). Similarly, the spin density values on Fe3 and Fe4 are similar (−0.52 e). As the spin multiplicity of the system increases, the Mulliken charge analysis indicates that the charges and spin densities around Fe and its surrounding O atom are redistributed accordingly. The spin density on Fe3 is 0.51, 1.15, 1.21, and...
2.61, while the spin density on Fe4 is estimated to be 0.56, 1.96, 3.57, and 3.64 for triplet, quintet, septet, and nonet states of CFO, respectively. The higher the spin multiplicity, the higher the density is located on Fe. Meanwhile, the spin density of the O7 atom remains to be around 1.0.


The geometry of Ca2Fe2O5 demonstrates that the Fe’s in the CFO are in the form of the tricoordinated tetrahedron. This structure, as well as the charge distributions, suggests that Fe is an active acceptor for the ligands such as CO. Therefore, we speculated that the coordination of the CO molecule on the Fe atom of CFO might be the first step of the Ca3Fe2O5-catalyzed conversion of CO/CO2. The catalyzed chemical looping of CO/CO2 on Ca3Fe2O5 is hypothesized as (a) CO adsorption on the Fe site of CFO, (b) O2 attachment to the Fe—O center of CFO, (c) CO + O2 → CO2 + O at the catalytic center of CFO, (d) CO adsorption to the activated Fe—O site, (e) CO conversion to CO2 at the activated Fe—O site, and (f) release of two CO2.

Table 3. Binding Energy and Free Energy (298 K) of the OC + CFO → OC—Fe Complex for Singlet, Triplet, Quintet, and Septet State Models

<table>
<thead>
<tr>
<th>State</th>
<th>singlet</th>
<th>triplet</th>
<th>quintet</th>
<th>septet</th>
</tr>
</thead>
<tbody>
<tr>
<td>E(OC—Fe complex) (au)</td>
<td>−4369.9017</td>
<td>−4369.9065</td>
<td>−4369.9069</td>
<td>−4369.8952</td>
</tr>
<tr>
<td>G(OC—Fe complex) (au)</td>
<td>−4369.9416</td>
<td>−4369.9473</td>
<td>−4369.9484</td>
<td>−4369.9373</td>
</tr>
<tr>
<td>ΔE (kcal/mol)</td>
<td>−38.7</td>
<td>−41.6</td>
<td>−40.5</td>
<td>−34.2</td>
</tr>
<tr>
<td>ΔG (kcal/mol)</td>
<td>−29.0</td>
<td>−31.8</td>
<td>−30.4</td>
<td>−55.8</td>
</tr>
</tbody>
</table>

ΔE = E(OC—Fe complex) − E(CFO) with E(CO) = −113.1286 au.

ΔG = G(OC—Fe complex) − G(CFO) with G(CO) = −113.1477 au.

Figure 4. Optimized structures of reactants, transition states, intermediates, and products for the triplet state and septet state (in italic) species (atomic distances in angstrom).
molecules at the catalytic center of CFO (Scheme 1). All the reactions take place on the CFO surface near the Fe site.

3.2.1. Coordination of CO to Fe of CFO. Attachment of the CO molecule to the CFO was found to form an OC–Fe(CFO) complex (P1, Figure 3) with the carbon atom coordinated to the Fe site. The corresponding C–Fe bond length varies from 1.75 Å (triplet) to 1.81 Å (septet). The related binding energy of this OC–Fe complex was computed to be around 40 kcal/mol. P1 has been located as a local minimum on the PES. The most stable state of the OC–Fe complex is identified as the quintet. Table 3 summarizes the binding energy of P1 in different spin states.

Table 4. Binding Energy and Free Energy (298 K) of the O2 + OC–Fe Complex → O2–OC–Fe Complex for the Triplet and Septet Models (in kcal/mol)∗

<table>
<thead>
<tr>
<th></th>
<th>triplet</th>
<th>septet</th>
</tr>
</thead>
<tbody>
<tr>
<td>E[O2–OC–Fe(CFO)]</td>
<td>−452.0326</td>
<td>−452.0202</td>
</tr>
<tr>
<td>G[O2–OC–Fe(CFO)]</td>
<td>−452.0748</td>
<td>−452.0637</td>
</tr>
<tr>
<td>ΔE (kcal/mol)</td>
<td>−4.29</td>
<td>−4.81</td>
</tr>
<tr>
<td>ΔG (kcal/mol)</td>
<td>−31.3</td>
<td>−36.1</td>
</tr>
</tbody>
</table>

“ΔE = E(O2–OC–Fe(CFO)) − E(O2) = E(OC–Fe(CFO)) − E(O2) − G(O2–OC–Fe complex) − G(O2) − G(OC–Fe complex) with G(O2) = −150.0777 au.

![HOMO-7 HOMO-6 HOMO-3 β-spin LUMO α-spin](image)

Figure 5. O2 unit-related π* MOs in the septet state. Only one of the π* orbitals of the O2 unit is unoccupied (LUMO).

Table 5. Energy Difference (ΔE) and Free Energy (ΔG, 298 K, in Brackets) for the Absorption of O2 on the Triplet and Septet State of P1 (in kcal/mol)

<table>
<thead>
<tr>
<th></th>
<th>triplet</th>
<th>septet</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2 + P1 → R2</td>
<td>−42.9(−31.3)</td>
<td>−48.1(−36.1)</td>
</tr>
<tr>
<td>R2 → P2</td>
<td>5.6(4.8)</td>
<td>6.0(5.5)</td>
</tr>
<tr>
<td>R2 → TS2</td>
<td>18.3(18.2)</td>
<td>15.5(15.2)</td>
</tr>
</tbody>
</table>

Table 6. Energy Difference (ΔE) and Free Energy (ΔG, 298 K, in Brackets) Values for the Absorption of O2 on the Triplet and Septet State of P1 (in kcal/mol)

<table>
<thead>
<tr>
<th></th>
<th>triplet</th>
<th>septet</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2 + P1 → R2</td>
<td>−42.9(−31.3)</td>
<td>−48.1(−36.1)</td>
</tr>
<tr>
<td>R2 → P2</td>
<td>5.6(4.8)</td>
<td>6.0(5.5)</td>
</tr>
<tr>
<td>R2 → TS2</td>
<td>18.3(18.2)</td>
<td>15.5(15.2)</td>
</tr>
<tr>
<td>P2 → P3</td>
<td>−9.3(−8.1)</td>
<td>−13.5(−12.8)</td>
</tr>
<tr>
<td>P2 → TS3</td>
<td>18.2(18.4)</td>
<td>16.9(17.2)</td>
</tr>
</tbody>
</table>

Table 7. Energy Difference (ΔE) and Free Energy (ΔG, 298 K, in Brackets) Values for CO2-Releasing Processes for the Triplet and Septet States (in kcal/mol)

<table>
<thead>
<tr>
<th></th>
<th>triplet</th>
<th>septet</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC + P3 → R4</td>
<td>−33.7(−23.4)</td>
<td>−16.3(−6.5)</td>
</tr>
<tr>
<td>R4 → P4</td>
<td>−89.6(−88.9)</td>
<td>−102.6(−102.3)</td>
</tr>
<tr>
<td>R4 → TS4</td>
<td>23.9(24.1)</td>
<td>10.9(10.2)</td>
</tr>
<tr>
<td>P4 → CFO + 2CO2</td>
<td>46.0(24.1)</td>
<td>32.8(42.7)</td>
</tr>
</tbody>
</table>

3.2.2. CO Conversion on the Quintet State of OC–Fe(CFO). 3.2.2.1. Absorption of O2 on the Quintet State of the OC–Fe(CFO) P1 Complex. It is noted that the O2 molecule has the electron triplet configuration in its ground state. When an oxygen molecule was introduced to the OC–Fe(CFO) complex in the quintet state, the spin multiplicity of the resulting complex CO–O2 should adopt either the triplet or septet state. The attachment of the O2 molecule is found to form an O12–Fe4–Fe3–O13 structure (R2) with an O12–Fe4 atomic distance of 1.91 Å (triplet) or 1.93 Å (septet) and an O13–Fe3 atomic distance of 1.98 Å (triplet) or 1.99 Å (septet). Thus, the O12–Fe4 interaction is slightly stronger than that of O13–Fe3 (see Figure 4). For the considered states (triplet and septet), R2 has been identified as a local minimum on the corresponding PES. The related binding energy amounts to −42.9 kcal/mol for the triplet state and −42.1 kcal/mol for the septet state (see Table 4).

It is important to note that in this attachment state (septet or triplet), one of the spin electrons on the Fe3 site has transferred to the O2 molecule. This can be seen from the Mulliken analysis. The spin density of Fe3 in R2 increases from 1.15 in P1 (quintet) to 1.82 for the septet and 1.88 for the triplet. There is one unpaired electron around the O–O moiety, and the total spin density on O12 and O13 is 0.79 in the R2 septet (−0.92 in the triplet, listed in Supporting Information). MO analysis (Figure 5) indicates that this unpaired electron occupies one of the π* antibonding orbitals of the O–O unit. Therefore, the corresponding O–O bond is activated by accepting an electron from the Fe site. As a result, the O–O bond elongates to 1.32 Å, about 0.13 Å longer than that of the isolated O2 molecule (1.19 Å, at the same level of theory) (shown in Figure 4).

Further exploration of the PESs of the CFO–CO–O2 complex results in another stable structure that indicates the absorption of O2 on the Fe4 site predominantly (P2, Figure 4). In view of the energy values, P2 is about 6.0 kcal/mol less stable than R2 for the septet state. Similarly, for the triplet state, P2 is about 5.6 kcal/mol less stable than R2. In this absorption structure, the O–O moiety mainly coordinates to the Fe4 site. For the septet states, the O–Fe4 atomic distance amounts to 1.92 Å for O12 and 1.97 Å for O13 in P2, while these distances are 1.91 Å for O12 and 2.63 Å for O13 in the O2-attached structure R2. Mulliken analysis reveals that in the presence of the coordinating interaction of the O–O moiety, Fe4 has a spin density of 1.0, therefore adopting the low spin state. Instead, without O–O coordination, Fe3 is characterized by the high spin, with a spin density of 2.6, which accounts approximately for three unpaired electrons. On the other hand, for the P2 triplet state, the O–Fe4 atomic distance amounts to 1.93 Å for O12 and 1.99 Å for O13, while these distances are 1.93 Å for O12 and 2.63 Å for O13 in the O2-attached structure R2. The corresponding spin density is 1.1 on Fe3 and 1.0 on Fe4. Both Fe3 and Fe4 adopt the low-spin configuration. Since the triplet is about 8 kcal/mol more stable than the septet, the low-spin configuration of Fe3 is more stable, as compared to the high-spin configuration in P2.

The transition state (TS2) between R2 and P2 was located for both the triplet and septet. Reaction coordinates from R2 to P2 were also calculated to ensure the proper assignment of the transition state (Figure 4). The energy barrier for this process is predicted to be 15.5 kcal/mol for the septet and 18.3
kcal/mol for the triplet state (Table 5). Thus, adsorption of O₂ on Fe₄ of the CFO−CO complex (in the quintet state) favors the septet state kinetically.

3.2.2.2. O−O Bond Dissociation and the Formation of CO₂. O−O bond dissociation and the establishment of the O−CO bond follow the formation of the O−O-activated compound P₂, resulting in a stable P₃ structure on the PES.

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Table 8. Energy Difference (ΔE) and Free Energy (ΔG, 298 K, in Brackets) Values for Releasing CO₂ from the Quintet State Complex (in kcal/mol)

<table>
<thead>
<tr>
<th></th>
<th>quintet</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ + P₁ → R₂</td>
<td>−42.6 (−30.8)</td>
</tr>
<tr>
<td>R₂ → P₂</td>
<td>12.6 (10.7)</td>
</tr>
<tr>
<td>R₂ → TS₂</td>
<td>16.7 (16.3)</td>
</tr>
<tr>
<td>P₂ → P₃</td>
<td>−16.5 (−14.2)</td>
</tr>
<tr>
<td>P₂ → TS₃</td>
<td>5.5 (7.1)</td>
</tr>
</tbody>
</table>

Table 9. Energy Difference (ΔE) and Free Energy (ΔG, 298 K, in Brackets) Values for the Absorption of CO on the Quintet State of P₃ (in kcal/mol)

<table>
<thead>
<tr>
<th></th>
<th>quintet</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC + P₃ → R₄</td>
<td>−22.1 (−11.9)</td>
</tr>
<tr>
<td>R₄ → P₄</td>
<td>−94.0 (−94.0)</td>
</tr>
<tr>
<td>R₄ → TS₄</td>
<td>19.0 (18.7)</td>
</tr>
<tr>
<td>P₄ → CFO + 2CO₂</td>
<td>37.3 (15.7)</td>
</tr>
</tbody>
</table>

A single atomic O and a bended O−C−O unit can be recognized in the complex P₃. Both O₁₃ and the C atoms of
the nonlinear $\text{O}−\text{C}−\text{O}$ coordinate to the Fe4 site. The O13–Fe4 atomic distance amounts to 1.83 Å and that of C–Fe4 amounts to 1.87 Å for the septet state (1.87 and 1.90 Å for the triplet, respectively). For the septet state, as compared to that of P2, P3 has been found to be about $−13.5 \text{ kcal/mol}$ more stable. Meanwhile, P3 is about $−9.3 \text{ kcal/mol}$ more stable than P2 in terms of energy in the triplet state (Table 6).

Transition state structures were located (TS3) for the corresponding P2 to P3 conversion on the PES for both triplet and septet states. The activation energy barriers of the transformation from P2 to P3 were calculated to be 16.9 and $18.2 \text{ kcal/mol}$ for the septet and triplet states, respectively. Kinetically, the septet state is favored for the O–O bond dissociation and the formation of O–CO bond steps.

3.2.3.3. Attachment of CO Associated with Releasing CO$_2$.

The bent form of the O–C–O moiety that appeared in P3 has been found not suitable to be released from the coordinated Fe4 site as the CO$_2$ molecule. We estimate that the activation energy of releasing a CO$_2$ molecule directly from P3 is expected to be higher than $60 \text{ kcal/mol}$. However, when an additional CO is attached to the complex P3, release of CO$_2$ from the CO–P3 complex becomes achievable.

Attachment of additional CO to the complex P3 results in an energetically stable intermediate R4, which corresponds to a local minimum structure on the related PES. The binding energy of the CO–P3 complex (R4) is $−9.8 \text{ kcal/mol}$ for the septet state and $−24.7 \text{ kcal/mol}$ for the triplet state. Large C–Fe atomic distances (3.29 Å for Fe4 and 4.42 Å for Fe3 in the septet and 3.36 Å for Fe4 and 4.51 Å for Fe3 in the triplet) also indicate the weak binding between CO and P3. An attack of the CO (from the C end) on the O atom (O13) of R4 leads to the formation of the second O–C–O unit in the complex, resulting in the P4 complex. Scanning the PES enables one to locate the corresponding transition state structure (TS4). The activation energy barrier of the creation of the O–C–O unit in this process is $17.9 \text{ kcal/mol}$ for the septet state. On the other hand, this energy barrier is $23.9 \text{ kcal/mol}$ for the triplet state. Thus, the reaction pathway along the triplet is less feasible. The energy difference between P4 and R4 amounts to $95.7 \text{ kcal/mol}$. A great amount of energy is released from the formation of P4. Since the absorption energy of 2CO$_2$ to the CFO core in the complex P4 is calculated to be $32.8 \text{ kcal/mol}$, the energy released from the process R4 $→$ P4 ensures the discharge of 2 CO$_2$ molecules from this 2CO$_2$–CFO complex P4 (Table 7).

It is important to note that based on the Mulliken population analysis, the spin density on the CFO moiety amounts to 0.6, divided among Fe4 (3.4), Fe3 (1.1), O7 (1.0), and O5 (0.4). Therefore, the CFO unit reconstructed from P4 is in the septet state.

3.2.3. CO Conversion on the Septet State of OC–Fe(CFO).

It should be noted that the spin multiplicity of the CFO released from the P4 is 7 (septet), while that of the CFO in the initial step of the reaction (step 2) is 5 (quintet). Therefore, the cyclic catalytic reaction mechanism for CO $→$ CO$_2$ is not completely described. To complete the cyclic catalytic reaction mechanism, further study should focus on the septet state of CFO. Coordination of CO to Fe of CFO in the septet state has been discussed above (Section 3.2.1). The following section starts discussion from the step of bringing the O$_2$ molecule to the OC–Fe complex (P1).

3.2.3.1. Absorption of O$_2$ on the Septet P1.

Bringing an oxygen molecule into the septet P1 results in the formation of the CFO–CO–O2 complex in the quintet state (nonet will not lead to the release of a quintet CFO expected for the cyclic catalytic process). The attachment of the O$_2$ molecule results in the formation of an O12–Fe4–Fe3–O13 structure (R2) with an O12–Fe4 atomic distance of 1.93 Å and an O13–Fe3 atomic distance of 1.98 Å (see Figure 6). R2 has been identified as a local minimum on the PES. The corresponding binding energy amounts to 42.6 kcal/mol. As a comparison, the corresponding value amounts to 42.1 kcal/mol for the septet state (see Table 5). This attachment causes migration of one of the spin electrons from the Fe3 site to the O2 molecule. As shown in the results of Mulliken population analysis, the spin density of Fe3 increases from 2.78 in P1 (septet) to 1.88 in R2 (quintet). Only one unpaired electron is located around the O–O moiety, and the total spin density on O12 and O13 amounts to $−0.90$ in R2 (quintet). MO analysis (Figure 7) indicates that this unpaired electron occupies one of the π* antibonding orbitals of the O–O unit. The corresponding O–O bond is activated by accepting an electron from the Fe site. Consequently, the O–O bond lengthens to 1.30 Å, about 0.11 Å longer than that of the isolated O$_2$ molecule (1.19 Å).

Search of the PESs of the CFO–CO–O2 complex leads to another local minimum structure that has the feature of the absorption of O$_2$ on Fe4 (P2, Figure 6). This local minimum structure P2 is about 12.6 kcal/mol over R2 in energy for the quintet state. The O–O moiety is largely coordinatened to the Fe4 site in P2. The O–F4 atomic distances amount to 1.85 Å for O12 and 1.87 Å for O13. As a comparison, these distances are 1.93 Å for O12 and 2.62 Å for O13 in the initial O$_2$ attachment structure R2. Mulliken population analysis reveals that in the presence of the coordinating interaction of the O–O moiety, the Fe4 has a spin density of 1.0, adopting the low spin state. However, without O–O coordination, Fe3 has the high spin feature, with a spin density of 2.0, due to approximately three unpaired electrons. On the other hand, the spin density on the O–O moiety is reduced to $−0.37$.

The transition state (TS2) between R2 and P2 was located for the quintet. Reaction coordinates from R2 to P2 were calculated to confirm that TS2 is the proper transition state (Figure 6). The energy barrier is predicted to be 16.7 kcal/mol for the R2 $→$ P2 conversion. Thus, adsorption of O$_2$ on Fe4 of the CFO–CO complex is achievable.

3.2.3.2. O–O Bond Dissociation and the Formation of CO$_2$.

The dissociation of the O–O bond and the establishment of the O–CO bond take place after the formation of the O–O–activated compound P2, resulting in a stable structure P3 on the PES. A single O atom and a bended O–C–O unit can be identified in the complex P3. Both O13 and the C atoms of the nonlinear O–C–O unit coordinate to the Fe4 site. The O13–Fe4 atomic distance amounts to 1.87 Å, and that of C–Fe4 amounts to 1.90 Å for the quintet state (Figure 6). Compared to that of P2, P3 has been found to be about $−16.5 \text{ kcal/mol}$ more stable. Mulliken population analysis reveals that Fe4 has a spin density of 1.6. On the other hand, the spin density on the Fe4 directly bonded to the O13 atom is reduced to $−0.06$.

The transition state structure was located (TS3) for the corresponding P2 to P3 conversion in the quintet state (Figure 6). The activation energy barrier of the transformation from P2 to P3 was calculated to be 5.5 kcal/mol (Table 8).

3.2.3.3. Release of CO$_2$ Associated with the Attachment of CO.

The direct release of the bent form of O–C–O from P3 in a form of the CO$_2$ molecule is difficult. The activation energy of directly releasing a CO$_2$ molecule from P3 was estimated to be higher than 80 kcal/mol in our testing.
computations. However, an additional CO attachment to complex P3 enables the detachment of CO$_2$ from the CO–P3 complex in the quintet state. This is a similar process to the case of the septet state discussed above.

Attachment of an extra CO to the P3 complex is viable. The resulting intermediate R4 is energetically stable, corresponding to a local minimum structure on the related PES. The binding energy of the CO–P3 complex is 12.7 kcal/mol for the quintet state. Large C–Fe atomic distances (3.25 Å for Fe4 and 4.48 Å for Fe3) suggest the weak binding between CO and P3.

Interaction between the C-end of CO and the atomic O (O13) in R4 leads to the creation of the second O–C–O unit in the complex, resulting in two CO$_2$-coordinated CFO units (P4, Figure 6). The transition state structure (TS4) corresponding to the R4 → P4 was located by scanning the PES of the quintet. The activation energy barrier of the formation of the O–C–O unit in this process is 19.0 kcal/mol. Thus, the reaction pathway along the quintet is feasible. The energy difference between P4 and R4 amounts to −94.0 kcal/mol. The binding energy of two CO$_2$ to the CFO core in the complex P4 is calculated to be 37.3 kcal/mol (Table 9).

Therefore, the energy released from the process R4 → P4 guarantees the release of two CO$_2$ molecules from the 2CO$_2$–CFO complex (P4). Mulliken population analysis demonstrates that the spin density on the CFO moiety amounts to 3.8, in which 1.7 is on Fe4, 1.0 is on Fe3, and 1.0 is on O7. Thus, the CFO unit freeing in this stage is in the quintet state.

4. CONCLUSIONS

A viable CFO catalytic reaction pathway of 2CO + O$_2$ → 2CO$_2$ conversion has been revealed based on the DFT computational investigations. It should be noted that Ca ions in the CFO are not involved in the catalytic processes directly. However, our initial study indicated that Ca ions are important in maintaining the local structure of the Fe-centered catalytic center. Moreover, the charge on the Ca ions is necessary for the charge balance in the units. Therefore, the intact CFO serves as a basic unit in the catalytic 2CO + O$_2$ → 2CO$_2$ conversion. The corresponding reaction is detailed in Scheme 2, and the reaction energy profile is summarized in Figure 8. In this pathway, one of the Fe centers in the catalyst CO → CO$_2$ conversion. Two energetically stable spin states of CFO, quintet and septet, provide compounds that serve as the effective catalyst. Due to the introduction of the triplet O$_2$ molecule, these two spin states convert along the catalytic reaction pathway. This pathway suggests a double release of the CO$_2$ reaction mechanism characterized by releasing two CO$_2$ molecules. The formation of the second CO$_2$ is sponsored by the existence of the CO$_2$ previously produced on the catalytic Fe center. Our results show that the rate-determining step is the formation of the 2CO$_2$–CFO complex (P4) in the quintet state (activation energy of 19.0 kcal/mol). The predicted energy barriers for all the steps suggest that the proposed pathway is plausible. On the other hand, a higher activation energy of the formation of P4 in the triplet state (23.9 kcal/mol) indicates that the pathway involving the triplet state is less favored. To verify the validity of this pathway, experimental studies of the corresponding reaction mechanism have been initiated.

ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jPCA.1c04431.

Corresponding orbitals of SMO for O7 of quintet CFO; Mulliken charge and spin density of all the related reactants, transition states, intermediates, and products and the full citation of ref 24 (PDF)

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