Aggregation and the Significant Difference in Reactivity therein: Blocking the CO₂ to CH₃OH Reaction

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ABSTRACT: A CoPc/CNT system was recently reported to transform CO₂ to methanol via electrochemical reductions, despite the catalyst has been studied since the 1980s, such observations were not reported earlier. A clue to the high methanol selectivity is that CoPc exist as mainly as monomers in the new report while in earlier works CoPc aggregates dominate. Here we have studied the reactivity of monomeric and dimeric CoPc by DFT. The mechanism involves rate limiting CO₂ association, with the C-O cleavage step being having very similar activation free energy. Once the Co-CO⁻ intermediate is formed the reaction bifurcates with two possible paths, CO dissociation or further reduction and protonation to give the Co-CHO⁻ intermediate, which then leads to methanol by further reactions. For the monomeric species at low reduction potentials CO dissociation is favored, but the formation of Co-CHO⁻ becomes competitive at more negative applied potentials. For the dimer the CO dissociation is always favored, and the reduction needed to form the C-H bond is negative enough for it not to be observed. The more difficult reduction stems from repulsive interactions between the Co-Pc units and lower solvent stabilization of the charge in the aggregate.

Introduction

The conversion of CO₂ into value-added product such as CO or methanol² is gaining more attention from the society as a result of the worsened environmental situation associated with high atmospheric CO₂ concentration¹ as well as the increasing demand for energy globally⁴. Electrochemical CO₂ reduction is of particular interest as it allows mild operating conditions, which potentially enable on-demand industrial operation² if stable and highly efficient catalysts are found. A wide selection of materials have been tested, ranging from transition metals such as copper⁹, silver or gold;⁹,10 organometallic catalysts with macrocyclic ligands⁹,10 or ter/bipyridine ligands¹¹ etc. Some molecular catalysts⁹,12 exhibit dramatically improved reactivity under heterogenous conditions when they are immobilised on a non-reacting carbon-based electrode and using water as the reaction medium. For example, in terms of turnover frequency (TOF), a dramatic increase of 3 orders of magnitude¹³ was observed for cobalt phthalocyanine (CoPc). As a heterogenous catalyst, it exhibits superior reactivity, good stability as well as low overpotential when compared to other hybrid catalysts. Moreover, it is the first transition metal complex reported that enables CO₂ to methanol reduction with good yields¹².

Hybrid molecular catalyst/carbon support materials rely on the π-π interactions between the catalyst and a carbon supporting material. However, such binding is by definition weak and low stability can limit larger scale production⁹,10. Our previous work on a Co(TPP)/carbon nantotube (CNT) system¹⁴ illustrated that flat catalysts tend to aggregate on CNTs as a result of stronger π-π interactions among the catalysts as compared to between the catalysts and the CNTs. Therefore, the curvature of the CNT plays an essential role in aggregation tendency: wider CNTs have better contact with the catalysts resulting in a reduced degree of aggregation. Apart from switching to flatter supporting materials, other proved methods that can minimise aggregation and hence improve TOF including (1) add bulky side groups to reduce the level or inter-catalyst π-π interactions; (2) grow a polymerised form of the catalyst¹⁵ on the CNT electrode, which can give as good TOF for CO₂ to CO conversion as the highly dispersed CoPc/CNT system; (3) incorporate the molecular catalyst in rigid structures such as metal organic frameworks (MOFs)¹⁶ or covalent organic frameworks (COFs)¹⁷. Furthermore, aggregation¹⁸ could in some cases block certain reaction pathways as demonstrated by Wang et al in a recent study¹². The sophisticated catalyst preparation method therein suggests that only when CoPc molecules are well dispersed, can methanol be obtained as the major product from CO₂ reduction at a relatively low reductive potential of -1.35V (vs. SHE). A few earlier reports¹⁹,20 together with some recent works²¹,22 of the same catalyst have only obtained trace amount of methanol (Faradaic Efficiency < 5%), if any. These observations highlight the importance of a highly dispersed system in CO₂ to methanol reduction.

Herein we present a computational study on the difference in reactivity between monomeric CoPc and dimeric CoPc, which is the simplest form of aggregates. In agreement with previous computational²³ and experimental studies²³, our results suggest that the catalyst-CO adduct is a key intermediate. We examined possible (further) reaction pathways of both monomer-CO and dimer-CO adducts, comparing reduction and
consecutive protonation, and the competing CO dissociation pathway which can limit further reduction to methanol.

Results and Discussions

Monomer Reactivity

We calculated the reductive potentials for the CoPc/CoPc$^-$ (-0.30V vs. SHE) and CoPc/CoPc$^{2-}$ (-0.96V vs. SHE) couple, which fit well with experimental measured reductive potentials obtained for a CoPc/graphite system (-0.34V, -0.71V) in water\textsuperscript{19}. In agreement with previous DFT\textsuperscript{25,27} and electron-spin resonance (ESR) spectroscopic studies\textsuperscript{25-27}, we confirmed that the unpaired electron resides in the metal d$_z^2$ orbital for CoPc (Figure 1a) and that the first reduction fills the metal d$_z^2$ orbital forming (CoPc)$^-$.

Molecular orbital (MO) analysis of (Co$^+$Pc)$^+$ suggests that upon the full-filling of d$_z^2$ orbital, its energy is lowered and the degenerate d$_{xz}$, d$_{yz}$ orbitals are now HOMOs. Since these three orbitals are very close in energy (Figure S1), shift in their alignment should be possible upon further reduction. The two degenerate LUMOs are ligand based but have some d$_{xz}/d_{yz}$ character.

The nature of the second reduction is less clear\textsuperscript{27,28,29}, ESR spectrum yields a narrow resonance close to 2.0023 (i.e. g factor for the free electron), suggests the doublet nature of (CoPc)$^{2-}$. However, no determine evidence exist in where exactly the unpaired electron locates. The twice reduces CoPc exhibits new absorptions in the 900-1100 nm region\textsuperscript{30} in the UV-vis spectrum, which was believed to be ligand based $\pi$-$\pi^*$ transitions, suggesting the reduction being ligand-based. One should also note that the disproportionation energies for (CoPc)$^{2-}$ is significantly lower than other MPcs where reductions are all ligand based, indicating the reversion back to Co$^0$ after the second reduction\textsuperscript{27}. We used both electronic structures as the initial guess and got (CoPc)$^{2-}$ with the unpaired electron in the previously fully occupied the d$_{xz}/d_{yz}$ orbital as the optimised configuration irrespectively (Figure 2b). This indicates a certain level of metal-to-ligand electron transfer (d$_{xz}/d_{yz} \rightarrow \pi$) and the twice reduced species exists as (Co$^0$Pc)$^\pi$, which is further evidenced by partial charge analysis – Co becomes more positively charged upon the second reduction (Table 1).

<table>
<thead>
<tr>
<th>Species</th>
<th>Co$^0$Pc</th>
<th>(Co$^+$Pc)$^-$</th>
<th>(Co$^+$Pc)$^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge</td>
<td>0.41</td>
<td>0.25</td>
<td>0.36</td>
</tr>
<tr>
<td>Spin</td>
<td>1.03</td>
<td>N/A</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Table 1. Mulliken partial charge and spin density analysis on the Co centre for relevant CoPc species

The calculated reaction profile at an applied potential of -1.04V (vs. SHE), which is the optimal reduction potential reported in experiment for CO production\textsuperscript{10}, is shown in Scheme 1. In line with an experimental study\textsuperscript{18}, our results indicate that CO$_2$ binding is the rate determining step. The calculated activation free energy of 16.7 kcal/mol is in very good agreement with experimental\textsuperscript{10} estimated value of 17.0 kcal/mol, which is converted from a TOF of 2.7s$^{-1}$ by transition state theory. CO$_2$ binding at the once reduced state as an alternative pathway is also possible as suggested by some studies\textsuperscript{18,23,31}, although it has to go through a slightly higher energy barrier (18.4 kcal/mol vs. 16.7 kcal/mol). Nonetheless, such difference is within the error range of DFT.

Upon CO$_2$ binding, d$_{z^2}$ electrons interact with an empty C sp$^2$ orbital, lowering the electron density on cobalt, which in turn leads to a charge transfer from the phthalocyanine ring back to the d$_{z^2}$ orbital. This re-generates Co$^0$ (Table 1) and leaving the unpaired electron on the phthalocyanine ring (Figure 3a). Upon protonation, CO$_2$ is further polarised strengthening the Co-C bond, shifting more electron density away from cobalt centre (Table 1). The unpaired electron remains on the phthalocyanine ring (Figure 3b) until the second proton attack, which triggers C-O bond cleavage and releases water. In the CoPc-CO complex the unpaired electron resides in the d$_{z^2}$ orbital to avoid excessive repulsion with the CO lone pair (Figure 3c). Moreover, the doubly occupied d$_{xz}$ and d$_{yz}$ can interact with CO via $\pi$ back-bonding. Thereafter, as in-line with previous theoretical studies\textsuperscript{25,32}, spontaneous CO dissociation regenerates Co$^0$Pc and closes the catalytic cycle.

Figure 1. The spin density of (a) CoPc and (b) CoPc$^{2-}$

Figure 2. (a) Orbital-alignment in (Co$^+$Pc)$^-$ and (b) the proposed orbital occupation for (CoPc)$^{2-}$

The nature of the second reduction is less clear\textsuperscript{27,28,29}, ESR spectrum yields a narrow resonance close to 2.0023 (i.e. g factor for the free electron), suggests the doublet nature of (CoPc)$^{2-}$. However, no determine evidence exist in where exactly the
which spontaneously bond with Co centre on the O site with protonation leads to $\text{CoPc}^{2-}$.

The same analyses were also performed for the di- and tri-oxides (Figure 2). At $-1.04\text{V vs. SHE}$, spontaneous GO dissociation is exergonic at both $-1.04\text{V}$ (vs. SHE) and $-1.34\text{V}$ (vs. SHE), while the preferred reaction afterwards is applied potential-dependent (Scheme 2). At $-1.04\text{V}$, spontaneous CO dissociation being the preferred pathway yielding ($\text{CoPc}$)$_2^-$, which is $-6.5\text{ kcal/mol}$ lower in free energy; while at $-1.34\text{V}$, we see a competition between CO dissociation (Scheme 2b, blue) and protonation (Scheme 2b, purple), explaining why a mixture of methanol and CO were obtained in the experiments.$^{12}$

A spin cross-over was observed for ($\text{CoPc}$)$_2^-$ as CO dissociates (Figure 4), which resulted in a kinetic barrier of $5.0\text{ kcal/mol}$. The same analysis was also performed for ($\text{CoPc}$)-CO, but no cross-over effect was observed (Figure S2).

Once the ($\text{CoPc}$)-CHO complex is obtained, an additional protonation leads to Co-C bond cleavage and releases HCHO, which spontaneously bond with Co centre on the O site with $\text{CoPc}^{2-}$.

According to our calculations, the next proton assisted reduction has an equilibrium reductive potential of $-1.47\text{V}$ which means that the intermediate formed is merely $2.5\text{ kcal/mol}$ higher in energy at $-1.34\text{V}$. The final proton assisted reduction ($-0.34\text{V}$) is very facile. It affords methanol and closes the catalytic cycle (Figure 5). Overall, the proposed mechanism for CO to then to methanol reduction agrees well with the experimental data available as discussed in the current section.
Dimer Reactivity

A dimer is the simplest form of aggregates. By exploring its reactivity, we can gain some insights into how aggregates differ from monomers in reactivity apart from the fact that not all active sites are accessible for CO\textsubscript{2} binding. In the case of CoPc, experimental results suggest that the monomer can further reduce CO to methanol while it is much less facile, if not impossible, for aggregates\textsuperscript{12}. It was previously proposed that the CoPc dimer exists in an eclipsed geometry as opposed to a metal-over-metal staggered fashion (Table S3)\textsuperscript{33,34}, to optimise the favourable electrostatic interactions while reducing the Pauli repulsion\textsuperscript{33}. Our DFT calculations suggest that the open shell singlet (Figure 6a) and the triplet state (Figure 6b) are very close in energy, as expected since the metals are well separated. Non-the-less, all spin alternatives were optimised, and the lowest energy spin-arrangement was selected for further investigation.

Figure 6. The geometry and spin density for (a) open shell singlet (CoPc)\textsubscript{2} and (b) triplet (CoPc)\textsubscript{2}

We applied the same analogy to dimers, and found out that after the first reduction, CO dissociation remains the preferred reaction pathway even at -1.34 V. Compared to monomers, the reductions are harder here due to a lower degree of solvation stabilisation (Table S10). Since the added charge is distributed on a larger system, it results in a lower charge density and hence weaker electrostatic interactions with water.

The negligible amount of methanol observed in previous studies at similar reductive potentials is likely produced by trace amount of monomeric CoPc presented in the system. In theory, a more negative applied potential can increase the driving force for proton assisted reduction and hence favours the formation of (CoPc)\textsubscript{2}-CHO, which is a key intermediate for methanol production. Nonetheless, one should also be aware that the added charge always acts as a competing reaction. Therefore, simply lowering the applied potential will not necessarily lead to a higher FE for methanol. In one study, where CO to methanol conversion (i.e. where CO dissociation route is suppressed) was studied\textsuperscript{21}, when applied potential was further lowered to -1.76 V (vs. SHE), hydrogen production dominates, and no methanol was detected.

The high electric field close to the electrode surface attracts protons as well as other cations in the solution resulting in higher local concentrations\textsuperscript{35} in a non-linear fashion. One can
imagine sites on larger aggregates are located slightly further away from the electrode surface where possibly experiences a lower proton activity than at the surface. This could be yet another reason making proton assisted reductions more difficult for aggregates, leaving spontaneous CO dissociation being the preferred reaction pathway. Furthermore, it is known that the presence of cation in an electric field stabilises the partial charges on the CO; oxygen atoms once it is activated, lowering the energy barrier for CO2 binding\(^5\). Hence CO2 binding may also be slightly harder for larger aggregates, highlighting the superior activity of monomeric CoPc.

The present study explored the reaction mechanism for monomeric and dimeric CoPc, and demonstrated that dimers are harder to reduce due to a less-degree of solvation stabilisation, leaving CO dissociation being the preferred reaction pathway. Our findings should in theory apply to larger aggregates as well. Built on our previous work Co(TPP) aggregates in a Co(TPP)/CNT system, the current work deepens our understanding on aggregate reactivity in heterogeneous catalysts and explained that the formation of aggregates can, in certain cases, block reaction pathways that may be desirable. We believe this finding is helpful for further catalyst design.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website.

Methodology, energies of optimized structures at different spin states, relevant analysis, relaxed coordinate scans for CO dissociation and solvation energy analysis (file type, PDF)

The optimized xyz coordinates of related species (file type, PDF)

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