Theoretical Study on the Degree of CO₂ Activation in CO₂-Coordinated Ni(0) Complexes

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ABSTRACT: The geometrical characteristic and the degree of CO₂ activation of the CO₂-coordinated Ni(0) complexes were investigated computationally by quantum chemical means for bidentate and tridentate ligands of PP, PPMeP, and PNP, and sometimes with co-complexing Fe(II) to differently coordinate CO₂. We show that the coordination geometry of the central metal is determined by the ligand geometry. The charge and the energy decomposition analyses show that the charge transfer energy through orbital mixing has a strong correlation with CO₂ net charge, while the binding energy cannot due to the lack of the coordination number and the deformation energy of the ligand. Among the examined ligands, PNP with negatively charged secondary amine makes Ni(0) an electron-rich atom, which results in an ∼20% higher CO₂ activation than those of PP and PPMeP. In particular, Fe(II)-PNP in the CO₂-bridged diatomic complex enhances CO₂ activation by another ∼20%, partly through the inductive effect of Fe(II), which pulls electron density from Ni-PNP across the CO₂-bridge and partly by the backward donation from Fe(II)-PNP. Therefore, the present study encourages us to design a strongly electron-donating ligand and a CO₂-bridged diatomic complex to develop more efficient homogeneous catalyst.

I. INTRODUCTION

As human civilization has continued to develop, energy consumption has increased exponentially, especially after the industrial revolution. Because this energy demand has mostly been met by burning carbonaceous fossil fuels such as oil, coal, and natural gas, the liberated carbon has increased the CO₂ level in the air, which is believed to be responsible for global warming and the ongoing climate disaster on this planet.1 As a result, developing renewable energies and related technologies for environmental protection has become an urgent and imminent issue. Although there are diverse approaches to mitigate the CO₂ level in the atmosphere, the most promising strategy is to reduce CO₂ to any form of a valuable material because carbon itself is also a necessary resource for energy circulation and sustaining the framework of organic substances.2 By chemical reduction, depending on the reduction pathway and the degree of reduction, CO₂ is converted into an energy resource such as CO, methanol, or methane. Many combinations of diverse metals and ligands have been studied in detail.7 Among them, Ni-cyclam8−12 (cyclam = 1,4,8,11-tetraazacyclotetradecan) and Fe- and Co-porphyrin families7 have shown interesting behaviors in terms of their performance and chemical mechanisms. Particularly in the cyclam series, [Ni(II)(cyclam)]Cl₂ showed superior performance to those of Co²⁺ and Fe²⁺ with a low bias of −1.05 V and higher CO selectivity.9,10 A mechanistic study by Song et al.1 revealed that Ni(II)(cyclam) is first bound to the electrode surface and reduced by one electron with −1.07 V (experimentally −1.23 V),12 Ni(I)(cyclam). This step is followed by thermoneutral CO₂ binding where CO₂ is reduced by one electron and Ni(I)

strategies of activating CO₂.6 In the homogeneous area, the molecular catalyst is solvated in a solution, normally in water, and it takes part in a catalyzing reaction in free solution or by being bound on the electrode surface. These catalysts are conventionally composed of a central metal (M), normally a transition metal (TM), and surrounding ligands. Carbon dioxide then adds to a vacancy in a metal atom or replaces a loosely bound ligand for further reaction. The most promising strategy is to reduce CO₂ to any form of a valuable material because carbon itself is also a necessary resource for energy circulation and sustaining the framework of organic substances.2 By chemical reduction, depending on the reduction pathway and the degree of reduction, CO₂ is converted into an energy resource such as CO, methanol, or methane. Many combinations of diverse metals and ligands have been studied in detail.7 Among them, Ni-cyclam8−12 (cyclam = 1,4,8,11-tetraazacyclotetradecan) and Fe- and Co-porphyrin families7 have shown interesting behaviors in terms of their performance and chemical mechanisms. Particularly in the cyclam series, [Ni(II)(cyclam)]Cl₂ showed superior performance to those of Co²⁺ and Fe²⁺ with a low bias of −1.05 V and higher CO selectivity.9,10 A mechanistic study by Song et al.1 revealed that Ni(II)(cyclam) is first bound to the electrode surface and reduced by one electron with −1.07 V (experimentally −1.23 V),12 Ni(I)(cyclam). This step is followed by thermoneutral CO₂ binding where CO₂ is reduced by one electron and Ni(I)

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Scheme 1. Schematic Presentation of Four Models

“The metallic oxidation number and total charge are denoted. R, R2, and R3 represent the methyl, isopropyl, and isobutyl groups, respectively.

is oxidized to Ni(II). In the whole catalytic reaction, the role of Ni(I) is crucial, as CO2 is attached to Ni(cyclam). Also, the amount of charge moving from Ni(I) to CO2 in this step would control the feasibility of the whole reduction mechanism.

The effect of the ligand was further studied experimentally by substituting H with a methyl group in the secondary amine position of the cyclam. The substitution lowered the overpotential compared to the pristine Ni(cyclam), but it enhanced the Gibbs energy of CO2 binding, which overall decreased the catalyst performance. The performance deterioration was ascribed to the thermodynamic stability of the CO2 adduct and its steric hindrance. Even though important insights have been drawn from these studies, many questions remain with regard to the characteristics of ligands (e.g., steric and/or inductive effect, roles of anchor atoms such as N, P, and S) and the central metals (e.g., the shape of d- and forbitals, HOMO-LUMO energy gap, and the oxidation state). In the case of polynedentate ligands, the coordination bond between the central metal and the coordinating atoms can be strained and affect the catalytic role.

Because the state of the central metal, Ni(I) in cyclam rather than Ni(II), is crucial for CO2 reduction, as stated above, the study for the low-valent metal-CO2 adducts has attracted much interest. After the characterization of (PCy3)2Ni(η2-CO2)13 (Cy = cyclohexyl) with zero-valent Ni, referred to as Ni0, many Ni-CO2 adducts with low valency were compounded.15 When the metal makes a coordination bond to C of CO2, Ni0 with large electron density can act as a strong nucleophile. Therefore, it is expected that the lower valent Ni will reduce CO2 much more and make it more feasible to reduce CO2 to other materials.

Recently, Lee’s group synthesized a series of CO2-coordinated Ni0 complexes where each ligand has a denticity of two or three for each Ni0 atom.16−19 Therefore, it is very heuristic to investigate the nature of Ni0-CO2 interaction systematically for this series. The models to be studied are represented in Scheme 1. The first model is (dtbpe)Ni-(η2-CO2) (dtbpe = 1,2-bis(di-tert-butylphosphino)ethane)18 denoted by 1-PP, where dtbpe is a bidentate neutral ligand with two P’s as anchor atoms. The second one is (PMe3P)Ni-(η2-CO2)16 denoted by 2-PMe3P, where PMe3P (PMMe3P = di-propylphosphino) is the modification of PP anion of bis(2-di-isopropylphosphino)phosphine as a tridentate ligand. Note that all P’s are tertiary phosphine excluding coordination to Ni. The third one is (PNP)Ni-η1-CO2-κ-C (PNP = N[2-PP2-4-Me-C6H4]2)19,21 denoted by 3-PNP, where PNP is an anionic ligand of the charge of −1. Note that the middle N in PNP is a secondary amine with two lone pairs, which results in a formal charge of −1. The fourth one is (PNP)Ni-μ-CO2-κ-C:κ-O-CO2-Fe(PNP)18 as denoted by 4-Ni-CO2-Fe, where two metal centers are bridged by CO2. This is a biomimetic complex of carbon monoxide dehydrogenase (CODH), which converts CO2 and CO reversibly.22,23 In the active site of CODH, CO2 is bridged between two metal centers of Ni and Fe (Ni-μ-CO2-κ-C:κ-O-CO2-Fe), as shown in Figure S1. Some calculations have been performed for a hypothetical model, as shown in Scheme S1, which replaces the middle P in 2-PMe3P with the tertiary N, referred to as 2’-PNMe3P, to understand the difference of the effects of the anchor atom species and its valence electrons. 2’-PNMe3P resembles 2-PMe3P with respect to the shape of valence electrons while it has the same anchor atom species as 3-PNP. We try to analyze the structural characteristics and the degree of CO2 activation for these models based on DFT calculations. For the estimation of the degree of CO2 activation, the electron charge density of CO2 is analyzed because the amount of electron charges on a CO2 molecule would facilitate the CO2 reduction reaction.

II. COMPUTATIONAL RESULTS AND DISCUSSION

For theoretical investigation, the hybrid density functional of B3LYP/6-31G(d) with dispersion correction24 equipped in Q-Chem25 was applied for geometry optimization, and the triple zeta basis set of G3Large was used for energy calculation. Each model was fully optimized, and the natural bond orbital (NBO)26 analysis was applied for the charge of metals (M = Ni, Fe) and CO2. The energy decomposition analysis (EDA)27 was done between the fragments of CO2 and the metal complex for each model. The charges and spin multiplicities used in the calculation are 0, 0 for Ni(0) and +2, 5 for Fe(II), and the overall charge of ligand PNP is −1, whereas all the other ligands are neutral.

a. Analysis of Geometry. The optimized structures are shown in Figure 1, and some geometrical parameters are summarized in Table 1. In Figure 1, H was removed, and C of ligands is drawn as a point for clear view. The full geometrical presentations including H are presented in Figure S2 in the Supporting Information.

Because there are so many CO2 adsorption modes for a single-atomic and diatomic catalyst, all the modes addressed in this work are presented in Figure S3. It is known that η1-C2O is the most stable for Ni0 without any ligands.28 The ground state of Ni0 with the coordination of a ligand is a singlet state of d19 (Table S1). As presented in the previous work, 1-PP and 2-PMe3P have η1-C2O mode as shown in Figure 1. While many CO2-adducts appear as η1-mode, it is known that some CO2-adducts have η1-C mode when a metal is in a relatively
Figure 1. The optimized structures of five models in Scheme 1 and Scheme S1 are drawn with the top view (top) and side view (bottom) using B3LYP/6-31G(d) + D. H’s are removed and some Cs in ligands are drawn as points for clarity. Color scheme: Ni, green; P, brown; C, black; O, red; N, blue; Fe, violet.

low oxidation state so that the energy of the d-orbital is relatively high, as well as when a central metal has a square planar or square pyramidal structure. Then, in 3-PNP, Ni2+ has square planar-like structure without CO2, which makes it prefer η1-C mode as shown in Figure 1. As for Fe(II) in model 4-Ni-CO2-Fe, it has η1,2O,2O′ mode with respect to CO2. Note that the charge of PNP-Fe is +1 as it is composed of Cl−. Hereafter, Ni(0)-PNP and Fe(II)-PNP without the coordination to CO2 are simply denoted as Ni-PNP and Fe-PNP, respectively, without any complexity in notation. The calculation shows that Fe2+ has a multiplicity of quintets with different metal complexes of Ni-PNP and Fe-PNP. Note that the charge of PNP-Fe is +1 as it is composed of Cl−. From the ligand field theory, NiII with a strongly donating ligand makes the electronic configuration of d7,10 which leaves sp3 orbitals for M-L (metal–ligand) coordination, resulting in a Td structure. Therefore, if the PNP ligand is replaced by three monodentate ligands such as two P(CH3)3 and one [NH2]+, it surely goes to a Td structure with η2-C,O mode for CO2 coordination, as shown in Figure 2d. Therefore, although NiII prefers a Td structure in its low oxidation state, when it is enforced to have a Td structure, for example, due to the constraint of the chelating PNP ligand, it favors the η1-C mode in CO2 binding.

In 4-Ni-CO2-Fe, CO2 is bridged by Ni-PNP and Fe-PNP in the type of μ-CO2-xC2-xC2O. This molecule is prepared by two different metal complexes of Ni-PNP and Fe-PNP. Note that although the coordination structure of Fe-PNP is PI in its optimized structure, it becomes Td in 4-Ni-CO2-Fe.

b. Analysis of Electronic Structure. To study the electronic properties of CO2-coordinated NiII complexes, the energy levels and the atomic basis coefficients of molecular

Table 1. Geometry Parameters for Models in Scheme 1 Using B3LYP/6-31G(d) + D

| parameters          | 1-PP | 2-PNP | 3-PNP | 4-Ni-CO2-Fe |
|---------------------|------|-------|-------|-------------|
| chg. mul            | 0, 1 | 0, 1  | −1, 1 | 0, 5        |
| geometry Ni         | PI (Pl)19 | Td (Td)16 | PI (Pl)19 | PI (Pl)18 |
| d(C–O) (Å)           | 1.289, 1.212 (1.266,1.200) | 1.252, 1.224 (1.252, 1.217) | 1.258, 1.257 (1.248, 1.247) | 1.318, 1.255 (1.289, 1.269) |
| d(Ni–C)              | 1.811 (1.868) | 1.875 (1.904) | 1.880 (1.911) | 1.844 (1.831) |
| d(Ni–O)              | 1.877 (1.904) | 2.234 (2.191) | 2.664 (2.614) | 2.856, 2.575 (2.705, 2.772) |
| O–C–O (°)           | 137.8 (138.0) | 133.4 (135.1) | 129.6 (128.5) | 118.4 (116.5) |
| O–Fe–O (°)          | 38.0 (61.0) | 58.0 (61.0) | 58.0 (61.0) | 58.0 (61.0) |

“The values in parenthesis are given from crystallography. PI and Td stand for planar and tetrahedral structures, respectively.”
Figure 2. The optimized ligand structure of (a) PPMeP, (b) PNMeP, and (c) PNP, and (d) structure of [Ni(0)(PCH3)2NH2]−1-CO2 calculated by B3LYP/6-31G(d) + D. In the ligand structures (a–c), H was removed for clarity. The black arrows denote the direction of the occupied molecular orbitals (MO) near the HOMO level, and the green triangle shows the ligand plane. The MOs in ligand structures are overlaid as much as the number of lone pairs. Colors scheme: Ni, green; C, gray; P, orange; N, blue; H, white; Fe, brown (drawn using Jmol).

Figure 3. (a) MO levels of 1-PP and its fragments of 1-PP-A and CO2 in fixed geometries. Only selected MOs are drawn, which are related to Ni and CO2. Representation of MOs of (b) HOMO of 1-PP-A (top view from z axis), (c) HOMO of 1-PP (side view from y axis), (d) LUMO+1 of 1-PP (slanted to view dxy-Ni), and (e) HOMO-7 of 1-PP. Colors scheme: Ni, green; C, gray; P, orange; N, blue; H, white (drawn using Jmol).

orbitals (MOs) were analyzed. The MO energy levels of 1-PP are shown in Figure 3a with its two fragments of CO2 (right side) and the Ni complex (left side) referred to as 1-PP-A in their fixed geometries. When a free CO2 is bent, the doubly degenerate HOMO ($\pi_{g}^{*}$, nonbonding orbital with 1 node) and LUMO ($\pi_{u}^{*}$, antibonding orbital with 2 nodes) levels are broken and the HOMO-LUMO gap is decreased as the HOMO level is increased and LUMO level is lowered, as shown in Figure S8. In the broken degeneracy, the MOs in the CO2 plane, also called in-plane mode, take up LUMO ($\pi_{g}^{*}$) and HOMO ($\pi_{u}^{*}$), while the MOs perpendicular to them, also called out-of-plane mode, are located at LUMO+1 ($\pi_{u}^{*}$) and HOMO-1 ($\pi_{g}^{*}$). In Figure 3a, the red lines denote the occupied orbital levels, and the blue ones denote the unoccupied orbital levels. In Figure 3a, only the selected MO levels are drawn, which are related to the atomic orbitals of Ni and CO2 for clarity. The green dashes denote the corresponding MOs between before and after CO2 coordination, which can be just the energy shift or an orbital interaction. All the levels and the relaxed structures of both fragments are shown in Figure S9. From the relaxed geometry to the fixed geometry (1st → 2nd and 5th → 4th column in Figure S9), the occupied levels are raised and the unoccupied levels are lowered around HOMO and LUMO levels, which explains the energetically unstable structure due to geometrical deformation. In the binding of 1-PP-A and CO2 in Figure 3a, the MO levels of Ni complex decrease while those of CO2 increase. This large shift of the energy levels is ascribed to the charge transfer from Ni to CO2, where the electron–electron repulsion energy is raised in CO2 and lowered in Ni. The backward donation normally occurs through the orbital interactions between LUMO of the bent CO2 ($\pi_{g}^{*}$) and any occupied orbitals of M complex, whereas the forward donation occurs through the orbital interactions between HOMO of the bent CO2 ($\pi_{u}^{*}$) and any unoccupied orbitals of M complex if it exists. In 1-PP, HOMO of 1-PP-A interacts with $\pi_{g}^{*}$ of CO2, which means that the backward donation occurs dominantly and is responsible for the CO2 activation.

The three occupied orbitals below HOMO in 1-PP-A mainly belong to Ni-3d orbitals but also include 4s, 4p orbitals due to the pre-existing coordination bond to P’s. HOMO of 1-PP-A is mainly composed of $d_{xy}$-Ni, as shown in Figure 3b. Note that the molecular ring is located on the xz plane. In Figure 3c, $\pi_{g}^{*}$-CO2 is well developed in HOMO of 1-PP, which comes from HOMO of 1-PP-A. Therefore, this demonstrates that $d_{xy}$-Ni charges are moved to the empty CO2 orbital, which confirms the backward donation of CO2. The correspondent antibonding appears in LUMO+1 as shown in Figure 3d, where the parity of CO2 is changed compared to Figure 3c, while the parity of $d_{xy}$-Ni remains the same. HOMO and HOMO-1 of the bent CO2 are located at HOMO-5 and -6 in 1-PP, respectively, which are just the shift of MO levels primarily due to the electrostatic effect ascribed to the increased charge density. Some complicated interactions appear as shown in Figure 3d and Figure S10; however, no trace of the forward donation was detected through MO analysis, so the binding of CO2 on Ni(0) occurs mainly through the backward donation.
Figure 4. (a) MO levels of 2-PPMeP and its fragments of 2-PPMeP-A and CO$_2$ in fixed geometries. Only selected MOs are drawn, which are related to Ni, and C and O in CO$_2$. Representation of MOs of (b) HOMO of 2-PPMeP-A, (c) HOMO of 2-PPMeP, (d) LUMO+5 of 2-PPMeP, and (e) HOMO-2 of 2-PPMeP. Colors scheme: Ni, green; C, gray; P, orange; N, blue; H, white (drawn using Jmol).

Figure 5. (a) MO levels of 3-PNP and its fragments of 3-PNP-A and CO$_2$ in fixed geometries. Only selected MOs are drawn, which are related to Ni and CO$_2$. Representation of MOs of (b) HOMO of 3-PNP-A, (c) HOMO of 3-PNP, (d) LUMO+5 of 3-PNP, and (e) HOMO-2 of 3-PNP. Colors scheme: Ni, green; C, gray; P, orange; N, blue; H, white (drawn using Jmol).

Figure 6. (a) MO levels of 4-Ni-CO$_2$-Fe and its fragments of 4-Ni-CO$_2$-Fe-A and CO$_2$ in fixed geometries. Only selected MOs are drawn, which are related to Ni, Fe, and C and O in CO2. Representation of MOs of (b) $\alpha$-HOMO-11, (c) $\alpha$-HOMO-2, (d) $\beta$-HOMO-6, and (e) $\beta$-LUMO+10 of 4-Ni-CO$_2$-Fe. Colors scheme: Ni, green; Fe, brown; C, gray; P, orange; N, blue; H, white (drawn using Jmol).
The MO levels of 2-PNMeP and its fragments of CO$_2$ and Ni complex (Ni-PNMeP-A) in fixed geometries are shown in Figure 4a, and there is not much difference from those of 1-PP. The overall molecular orbital levels including the relaxed geometries are also presented in Figure S11. In Figure 4a, there appears backward donation of CO$_2$ with d$_{z^2}$ and d$_{xy}$ in HOMO and HOMO-2 of 2-PNMeP-A, respectively. Then, the bonding and antibonding orbitals are shown in Figure 4c,d, and another backward donation at HOMO-2 in 2-PNMeP is detected Figure 4e.

The substitution of the tertiary P with the tertiary N for 2'-PNP does not make a significant difference, as shown in Figure S12, as expected through the similar valence electron structure. However, the secondary N-substitution effect on MO levels in 3-PNP is significant as shown in Figure 5a. The HOMO level of 3-PNP-A is much higher than the level of Ni-PNP stays at a similar energy level. The MO level difference between HOMO of 3-PNP-A and LUMO of CO$_2$ reaches 0.198 Hartree, which is much larger than those of 0.025–0.043 Hartree for the previous models. Therefore, this large energy difference can be a driving force for charge transfer from Ni complex to CO$_2$. Due to the high energy of HOMO, PNP itself has a strong tendency to donate electrons when combined with any other molecule. Therefore, any M-PNP complex is expected to have a strong tendency to donate electrons when any molecule is coordinated to the central metal. Figure 5b shows HOMO of d$_{x^2-y^2}$ of 3-PNP-A, which interacts with $\pi^*_{p}$-CO$_2$. The bonding and antibonding orbitals are drawn in Figure 5c,d, and another backward donation appear, as shown in Figure 5e.

Lastly, MO levels of the CO$_2$-bridged bimetal complex of 4-Ni-CO$_2$-Fe are presented in Figure 6a with those of its fragments in the fixed geometries. The green lines represent only the backward donations between metals and CO$_2$. As for 4-Ni-CO$_2$-Fe-A, two separate molecules of Ni-PNP and Fe-PNP exist, so they were calculated together as a supramolecule, as shown in Figure S14. The MO splitting in Figure 6a shows that both $\alpha$- and $\beta$-spin contribute to the backward donation to CO$_2$. In the bonding orbital of $\alpha$-HOMO-11, two MOs from 4-Ni-CO$_2$-Fe-A contribute, one from Ni (HOMO-3) and the other from Fe (HOMO-5). The bonding and antibonding orbitals for $\alpha$-spin are drawn in Figure 6b,c. In the $\alpha$-bonding orbital, the C$_p$ orbital of $\pi^*_{p}$-CO$_2$ bonds with Ni-d$_{x^2-y^2}$ while one of two O-pz’s of $\pi^*_{p}$-CO$_2$ interacts with the Fe-d$_{xy}$ orbital.

Considering the parity of the Fe-d$_{xy}$ orbital and $\pi^*_{p}$-CO$_2$ only one O1-p$_{o}$ orbital (blue color) can overlap with the d-orbital of Fe (blue color) because the other O2-p$_{o}$ (blue color) has the opposite parity to Fe (red color), as shown in Figure 6b. Therefore, we can say that some portion of the backward donation can occur through the Fe-PNP complex when co-complexing CO$_2$ in $\pi$O2O’ mode. Note that the $\alpha$-spin is fully occupied in high spin of Fe$^{2+}$, even though the d-orbital is not fully occupied. As for $\beta$-spin, the considerable backward donation appears only through Ni, as shown in Figure 6d. Because Fe$^{2+}$ has only one electron of $\beta$-spin in high spin configuration, no meaningful backward donation occurs from Fe$^{2+}$. Resultantly, Fe(II)-PNP partly contributes to the backward donation to CO$_2$ in a concerted mode with Ni$^0$ in its high spin configuration.

**c. Charge and Energy Decomposition Analysis.** Energy decomposition analysis (EDA) was done and displayed in Figure 7a for the five models in Scheme 1 and Scheme S1. In Figure 7a, FRZ of EDA components stands for the electrostatic repulsion energy attributed to the frozen electron density when two fragments of CO$_2$ and the Ni complex are combined in the fixed geometries. POL is the polarization energy through intrafragment relaxation from the frozen density, and CT is due to the interfragment electronic relaxation of MOs. Note that FRZ makes the system unstable while POL and CT make the system stable, so FRZ has an opposite sign. In Figure 7a, FRZ reversed for comparison. The total SCF energy is largely a sum of CT, POL, and -FRZ. Considering the relative energy differences between models in FRZ and POL counterbalance each other; thus, SCF resembles CT.

Therefore, the SCF energy is largely affected by the CT energy, which comes from the charge delocalization. Because the CO$_2$ binding occurs mainly through the backward donation, CT and BE are expected to be aligned. However, by definition, BE includes the deformation energy of each fragment with reference to the fully relaxed structures of each fragment, which is different from SCF TOTAL in EDA. BE in Figure S15a increases from 2-PPMeP$^3$ to 4-Ni-CO$_2$-Fe.
smoothly. However, the abnormally high BE of 1-PP is ascribed to the lack of coordination bonds to Ni, which increased POL in Figure 7a. The difference between SCF and BE is much more for 4-Ni-CO2-Fe, where the coordination geometry of Fe-PNP changes greatly from Pl to Td. This deformation energy abruptly reduced the BE of geometry of Fe-PNP changes greatly from Pl to Td. This means Fe2+ strengthens the electron donation of Ni-PNP to Fe. Colors scheme: Ni, green; C, gray; P, orange; N, blue; Fe, brown.

Table 2. Partial Charges from Natural Atomic Orbital Analysis

| models       | CO2  | Ni0 | $\Delta$Ni0 | $\Delta$(Ni0,A’s) | Fe2+ | $\Delta$Fe2+ | $\Delta$(Fe2+,A’s) |
|--------------|------|-----|-------------|-------------------|------|-------------|-------------------|
| 1-PP         | −0.812 | 0.804 | 0.334 | 0.588 | N/A | N/A | 1.424 | 0.147 | 0.143 |
| 2-PPMeP      | −0.793 | 0.862 | 0.215 | 0.556 | N/A | N/A | 1.042 | 0.142 | 0.143 |
| 3-PNP        | −1.044 | 0.792 | 0.318 | 0.729 | N/A | N/A | 1.046 | 0.142 | 0.143 |
| 4-Ni-CO2-Fe  | −1.214 | 0.908 | 0.434 | 0.884 | 1.424 | 0.147 | 0.143 |

$\Delta$M and $\Delta$(M,A’s) stand for the difference of atomic charges after CO2 coordination for M and the sum of M and the anchor atoms (A’s) of the ligand, respectively. The reference charges are 0.474 for Ni0 and 1.277 for Fe2+ in M complex without CO2.

Figure 8. Atomic charges from natural atomic orbitals for (a) 2-PPMeP-A, (b) 2-PPMeP, (c) 3-PNP-A, (d) 3-PNP, (e) Fe-PNP, and (f) 4-Ni-CO2-Fe. Colors scheme: Ni, green; C, gray; P, orange; N, blue; Fe, brown.
PNP has relatively lower partial charge due to the PNP ligand, compared to Fe2+ with neutral ligands. Therefore, some extra electron charges of Fe2+ in Fe-PNP can be donated to CO2 through the backward donation as was examined in MO analysis previously. Therefore, though Fe2+ is Lewis acidic, when it is combined with an electron-rich ligand such as PNP(−1), the backward donation from Fe2+ to CO2 can occur. Accordingly, Fe-PNP coordinated to CO2 with χO2O’ mode can activate CO2 through two methods: (1) by inductively attracting the electrons from the Ni-PNP side and (2) by directly donating the electron charges from itself.

III. CONCLUSIONS

We investigated the nature of CO2 binding on four Ni(0) complexes: 1-PP (η1-CO2), 2-PP(Ni-PNP) (η1-CO2), 3-PP(Ni-PNP) (η1-CO2), and 4-Ni-CO2-Fe (μ-CO2-κ-C:χO2O’). The DFT calculations in the regime of B3LYP/6-31G(d) + D accurately reproduced the coordination geometries of the central metals, where PP(Ni-PNP) ligand induces the tetrahedral structure (Td) of Ni and PNP ligand induces planar structure (P1). Although the ligand field theory predicts that Ni5+ prefers Td, the geometry of the chelating ligand enforces the coordination geometry of metal, where PP(Ni-PNP) leads to Td and PNP leads to P1. As for CO2 binding mode, normally CO2 is strongly bound to the central metal in η2-mode, but planar structure of Ni5−PNP complex prefers η1-C mode.

Based on the analysis of molecular orbitals, the backward donation to LUMO of the bent CO2 is mainly responsible for the CO2 binding, which is also responsible for the degree of CO2 activation. However, the binding energy (BE), although it comes from backward donation, cannot precisely explain the degree of CO2 activation because the coordination number and the deformation of ligand do affect BE. Otherwise, the charges of CO2 show strong correlation with the charge transfer (CT) energy from the energy decomposition analysis (EDA). Compared to 1-PP and 2-PP(Ni-PNP), 3-PP shows a largely increased CO2 charge of about 0.2e due to the negatively charged [PNP]−ligand. Ni5+ with the coordination to PNP is already in an electron-rich state, so it can activate any adsorbate such as CO2. In the diatomic complex of 4-Ni-CO2-Fe, an additional charge transfer of about 0.2e occurs. Interestingly, after the coordination of Fe-PNP to 3-PNP with χO2O’ mode, Fe(II) pulls the electron density from Ni-PNP across the CO2 bridge, which enhances the backward donation from Ni-PNP to CO2. Furthermore, Fe(II) also donates some charge from itself to CO2 through the backward donation mechanism. So, the resultant increased charge on CO2 comes partly from the inductive effect of Fe(II) and partly from the backward donation ascribed to PNP in Fe-PNP complex. Therefore, this finding gives insight to designing a new catalyst and explains why we should aim at the diatomic catalyst for CO2 reduction.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c06257.

The details of the geometry of models, MO levels of Ni(0) atom, ligands, and models, multiplicity of Ni5+ and Fe2+, and their complexes, BE and SCF of EDA, and NBO analysis (PDF)

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Notes

The authors declare no competing financial interest.

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