The Active Center of Co−N−C Electrocatalysts for the Selective Reduction of CO₂ to CO Using a Nafion-H Electrolyte in the Gas Phase

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ABSTRACT: To contribute a solution for the global warming problem, the selective electrochemical reduction of CO₂ to CO was studied in the gas phase using a [CO₂(g), Co−N−C cathode | Nafion-H | Pt/C anode, H₂/water] system without using carbonate solutions. The Co−N−C electrocatalysts were synthesized by partial pyrolysis of precursors in inert gas, which were prepared from various N-bidentate ligands, Co(NO₃)₂, and Ketjenblack (KB). The most active electrocatalyst was Co−(4,4′-dimethyl-2,2′-bipyridine)/KB pyrolyzed at 673 K, denoted Co−4,4′-dmbpy/KB(673K). A high performance of CO formation (331 μmol h⁻¹ cm⁻², 217 TOF h⁻¹) at 0.020 A cm⁻² with 78% current efficiency was obtained at −0.75 V (SHE) and 273 K under strong acidic conditions of Nafion-H. Characterization studies using extended X-ray absorption fine structure (EXAFS), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy−energy-dispersive X-ray (TEM-EDX), X-ray diffraction (XRD), and temperature-programmed desorption with mass spectrometry (TPD-MS) indicated the active site as Co coordinated with four N atoms bonding the surface of KB, abbreviated Co−N₄−Cₓ structure. A model of the reduction mechanism of CO₂ on the active site was proposed.

1. INTRODUCTION

Recycling CO₂ as an energy carrier of the renewable energy by the conversion of CO₂ to useful chemicals such as CO, methanol, alkenes, higher hydrocarbons, etc., is promising for the reduction of the CO₂ emission and also for the break from the dependency on petroleum resources. Attractive methods of the CO₂ reduction have been proposed using heterogeneous catalytic,¹−³ photochemical,⁴−⁶ biochemical,¹² and electrochemical reactions.⁸−¹² Strong points of the electrochemical reduction of CO₂ are (i) to directly apply renewable electricity such as solar and wind power, (ii) to use various proton sources such as water, alcohol, hydrogen, and so on, (iii) to easily control reaction rates by a cathode potential, and (iv) to operate the reaction under mild conditions.

Our target product is CO, which is an industrial major material into a lot of useful chemicals and is a reductant for iron making.¹² A standard potential between CO₂ and CO (eq 1) is slightly negative than that between H⁺ and H₂ (eq 2). A good reductant of CO can function as a useful intermediate material in chemical processes. The rate-determining step in eq 1 has been proposed to be the one-electron reduction of CO₂ to CO₂⁻ having a more negative reduction potential (eq 3). Although a potential of the second one-electron reduction is more positive (eq 4), it is considered that the total reaction rate of eq 1 is slow.⁸⁻⁹

[\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{CO} + \text{H}_2\text{O}^{\circ}\text{SHE} = -0.11 \text{V}} \hspace{1cm} (1)
[\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \hspace{0.5cm} \text{E}^\circ = 0.00 \text{V SHE}} \hspace{1cm} (2)
[\text{CO}_2 + \text{e}^- \rightarrow \text{CO}_2^- \hspace{0.5cm} \text{E}^\circ = -1.93 \text{V SHE}} \hspace{1cm} (3)
[\text{CO}_2^- + \text{e}^- + 2\text{H}^+ \rightarrow \text{CO} + \text{H}_2\text{O}^{\circ}\text{SHE} = +1.71 \text{V}} \hspace{1cm} (4)

Hydrogen evolution reaction occurs easily (eq 2) to compare with the rate-determining-step (eq 3) in general systems for the CO₂ reduction. A suppression of the H₂ evolution is key to achieve the selective reduction of CO₂ to CO. Therefore, carbonate solutions saturated CO₂ at higher pH are usually used as favorable electrolyte solutions for the reduction of CO₂ with suppressing the evolution of H₂ (E°/V = 0.00−0.059 pH). Hori and co-workers have done many attractive works using various metal electrodes for the electroreduction of CO₂ in carbonate...
aqueous solutions and found active metal electrodes such as Cu, Au, Ag, and Zn.13–19

If we want to realize a fast electroreduction of the CO₂ conversion, a concentration of CO₂ in carbonate aqueous solutions should control the reduction rate of CO₂ as equal to the current density because of the low solubility of CO₂ in water (34 mM).20 A gas-electrolysis cell using gas diffusion electrodes (GDEs) should be employed for a fast-electrochemical reaction.21–30 Gaseous CO₂ is directly reduced on a GDE. Our research group has reported electrosynthesis in the gas phase, which has advantages to achieve a higher formation rate and selectivity of useful chemicals.31,32 When a GDE connected with Nafton-H membrane as an electrolyte is employed for the CO₂ reduction, most of the active electrocatalysts such as metallic Cu and Ag nanomaterials studied in carbonate solutions cannot work for the reduction using the Nafton-H membrane without carbonate solutions.18,19 Because the acidity of the Nafton-H membrane is too strong, the evolution of H₂ dominantly proceeds during the CO₂ electroreduction and the Cu and Ag electrocatalysts dissolve into Nafton-H. Therefore, most of the works using the metal nanoparticle electrocatalyst deposited on GDEs employed ion-exchange membranes and carbonate solutions or KOH solutions. Very good performances for the reduction of CO₂ to CO, CH₄, or C₂H₄ have been achieved, though their cathode potentials were very negative, less than −1.0 V (SHE).21–30 Significant amounts of carbonate or KOH solutions have to circulate for the electrolysis operation, and a large amount of CO₂ dissolves in the solutions. This is a serious disadvantage to put to a practical process. Therefore, new electrocatalysts working on the GDE without using carbonate or KOH solutions should be developed for the electroreduction of CO₂ in the gas phase.

We have recently reported new electrocatalysts prepared from Co(NO₃)₂, N-bidentate ligands, and carbon powder (KB; Ketjenblack) for the reduction of CO₂ to CO by a gas-electrolysis cell using Nafton-H.33,34 Strasser et al. have reported similar electrocatalysts of M−N−C (M: Ni, Fe, Mn, Cu, Co) prepared from polyaniline, metal chlorides, and KB for the reduction of CO₂ to CO and CH₄ using carbonate and KOH solutions.39,40 Especially, the Ni−N−C electrocatalyst on GDE is very active for the CO₂ reduction using carbonate and KOH solutions; however, the electrocatalysts do not work for the reduction of CO₂ but remarkably promote H₂ formation in acidic conditions.59,60 In contrast, our electrocatalysts can work for the CO₂ reduction under strong acid conditions of Nafton-H without using any carbonate, KOH, and salt solutions, as shown in Figure 1.33,34 This is the particular electrocatalysis to compare with other electrocatalysts.31–30

A partial pyrolysis treatment of a raw material of Co(NO₃)₂, N-bidentate ligands, and KB is essential for the preparation of an effective electrocatalyst denoted Co−N−C electrocatalyst. A lot of N-bidentate ligands for Co were screened in the previous work, and several effective ligands were found; especially, 4,4′-dimethyl-2,2′-bipyridine (4,4′-dmbpy) showed a highest current efficiency of 75% with a good formation rate at −0.70 V (SHE).33 Therefore, we focused on the selective electrocatalysis of the partial pyrolyzed Co(NO₃)₂−4,4′-dmbpy/KB materials for the reduction and reported the basic kinetics and electrocatalysis in the previous studies.33,53 However, on the basis of the formation rate of CO, effective N-bidentate ligands were 6,6′-diamino-2,2′-bipyridine (6,6′-dabpy) and 4,4′-di-tert-butyl-2,2′-bipyridine (4,4′-dtBubpy), though their current efficiency were lower than that of 4,4′-dmbpy.53

![Figure 1](https://dx.doi.org/10.1021/acs omega.0c01510)

**Figure 1.** Schematic diagram of electroreduction of CO₂(g) using a [Co−N−C cathode | Nafton-117 | Pt/KB anode] electrolysis cell.

Purposes of this work are (i) to evaluate the electrocatalysis of the Co−N−C compounds prepared from 6,6′-dabpy, 4,4′-dmbpy, other N-bidentate ligands, and the 4,4′-dmbpy ligand to clarify the most effective electrocatalyst and (ii) to reveal a structure of the active site and a reaction mechanism of the CO₂ reduction over the Co−N−C catalyst by characterization studies.

2. RESULTS AND DISCUSSION

2.1. **Effects of N-Bidentate Ligands to Co.** Previously, we have compared various Co−N-bidentate-ligands/KB electrocatalysts activated at 573 K and chose the 4,4′-dimethyl-2,2′-bipyridine ligand as the best one based on a CE(CO).33,34 However, we did not confirm influences of pyrolysis temperatures of other Co−ligand/KB precursors. Therefore, effects of pyrolysis temperatures of seven precursors using ligands of 1: bpy, 2: 4,4′-dmbpy, 3: 5,5′-dmbpy, 4: 6,6′-dmbpy, 5: 6,6′-dabpy, 6: 4,4′-dtBubpy, and 7: phen were studied.

When the pyrolysis temperature was 573 K, good reproducibility of the electrocatalysts for the CO₂ reduction was obtained.33 The order of ligands based on the CE(CO) was 2 (80%) > 3 (70) > 6 (55) > 5 (40) > 1 (39), 4 (39) > 7 (38) at −0.70 V. To focus on the FR(CO), the order was 5 (240 μmol h⁻¹ cm⁻²) > 6 (100) > 2 (60) > 3 (45) > 4 (40) > 1 (35), 7 (35). The 5 and 6 ligands were more active than the 2 ligand. Therefore, we focused on the CEs(CO) and FRs(CO).

Figure 2 shows the effects of pyrolysis temperatures of the various electrocatalyst precursors on the electroreduction of CO₂ at −0.70 V(SHE). The major products were CO and H₂, and the sum of CE(CO) and CE(H₂) was approximately 100%. A trace amount of CH₄ was detected; however, CH₄ was a minor product and a CE(CH₄) was less than 0.5%. Therefore, we focused on only the CO formation in this work.

When the pyrolysis temperature of the precursors was raised from 573 to 673 K, the order based on the FRs(CO) changed from 5 > 6 > 2 > 3 > 4 > 1,7 at 573 K to 2 > 3 > 6 > 4 > 5 > 1 > 7 at 673 K. On the other hand, the order based on the CEs(CO) changed from 2 > 3 > 6 > 5 > 1, 4 > 7 at 573 K to 2 > 3 > 6 > 4, 1 > 7 > 5 at 673 K. At a higher pyrolysis temperature of 773 K for the precursors, the FRs(CO) slightly decreased and the CEs(CO) drastically decreased because of steep increases in the j values due to an acceleration of H₂ formation.

Herein, the 2 ligand showed excellent function for the acceleration on both CE(CO) and FR(CO), but the 5 and 6 ligands were not under higher temperature activation at 673 K. The Co−2-ligand/KB(673K) electrocatalyst showed the maximum FR(CO) of 253 μmol h⁻¹ cm⁻² with a high CE(CO) of 79%. At a lower pyrolysis temperature at 473 K, electro-
precursors on their electrocatalysis for CO₂ reduction: (a) CO₂: 1 atm (10 mL min⁻¹) ligand/KB (18 mg) + VGCF (30 mg) + PTFE powder (3 mg), anode: 5 M ligand showed a different property on pyrolysis temperatures (Co−ligand/KB(473K) materials disappeared, indicating no formation of CO and H₂. As can be noticed, the Co−ligand/KB (573K) electrocatalysts were very good; therefore, we focused on the Co−ligand/KB(573K) electrocatalysts. The FRs(CO) at the Co−2-ligand/KB(673K) and Co−5-ligand/KB(573K) electrocatalysts were very good; therefore, we focused on the Co−2-ligand/KB(673K) and Co−5-ligand/KB(573K) electrocatalysts. The j values and FRs(CO) increased with a decrease in cathode potential on both electrocatalysts. The CE(CO) for the Co−2-ligand/KB(673K) electrocatalyst was almost constant between −0.55 and −0.70 V, whereas that for the Co−5-ligand/KB(573K) electrocatalyst increased with a decrease in potential. Although maxima FRs(CO) for both electrocatalysts were almost the same values at −0.75 V, the CE(CO) of 78% for the Co−2-ligand/KB(673K) electrocatalyst was much higher than that of 34% for the Co−5-ligand/KB(573K) electrocatalyst. Figure S1 in the Supporting Information shows time courses of the electroreduction of CO₂ by using a fresh Co−2-ligand/KB(673K) electrocatalyst at −0.75 V and 273 K. In the early stage of the reaction for 60 min, gradual decreases in j, FR(CO), and CE(CO) were observed; however, electroreduction activities were stable after 60–240 min. The turnover number of Co on the formation of CO for 240 min was 5.35 × 10⁴ times. This indicated that the Co−2-ligand/KB(673K) electrocatalyst was stable and active for the reduction under our reaction conditions. We could conclude that the 2 ligand was more efficient than the 5 ligand.

2.2. Activation Process of Co−4,4′-dmbpy/KB. As described above, the 2 ligand (4,4′-dmbpy) was the most effective for the Co−ligand/KB(673K) electrocatalysts. The heat treatment of the Co−4,4′-dmbpy/KB precursor is an essential process for the generation of the active site for the electroreduction of CO₂, as shown in Figure 2. To clarify the thermal decomposition processes, products (m/z values: parent signal and fragment signals) from the precursors were observed. Figure 4 shows TPD-MS profiles of 1wt%Co−4,4′-dmbpy/KB. Reference TPD-MS profiles of KB, 4,4′-dmbpy, Co(NO₃)₂.
6H₂O/KB, and 4,4′-dmbpy/KB are indicated in Figure S2 of the Supporting Information. Focusing on the reference profiles, the decomposition peak of Co(NO₃)₂·6H₂O/KB was first detected at 490 K, as shown in Figure S2c; the main products were H₂O (m/z = 18), NO (30, (14)), and CO₂ (44, (12, 16, 28)). Co(NO₃)₂·6H₂O decomposed to H₂O, NO, and CoO. At 790 K, the evolution of CO (28, (12)), CO, and CO₂ are likely to evolve during the reduction of CoO₃ to Co by a carbon support. Note that any thermal decomposition products were not detected for the profile of the KB support at <1000 K, as shown in Figure S2a. In the profile of 4,4′-dmbpy/KB in Figure S2d, no Co, the thermal decomposition of 4,4′-dmbpy was observed from 600 K. In addition to H₂ (m/z = 2) and H₂O desorption, significant signals assigned to hydrocarbons, m/z = 14 (CH₄), 15 (CH₃), 16 (CH₄), 27 (C₂H₃), 28 (C₂H₄), and 29 (C₂H₅), were observed. The 4,4′-dmbpy ligand decomposed at 600–700 K, desorption of CH₄ (16, (15)) at 750–900 K, and desorption of C₂ hydrocarbons at >850 K (28 (27)). It is noted that a pure 4,4′-dmbpy reagent showed no decomposition products at <1200 K because of the evaporation of 4,4′-dmbpy, as shown in Figure S2b. Thus, 4,4′-dmbpy strongly adsorbed on the KB support or immobilized on the surface.

The decomposition profile of 1wt%Co–4,4′-dmbpy/KB is shown in Figure 4. The desorption signals assigned to NO, H₂O, and CO₂ were observed at 500 K, corresponding to the decomposition of nitrate, as shown in Figure S2c. Over 550 K, desorption signals assigned to H₂, CH₄, CO₂, and C₂ hydrocarbons were detected, similar to Figure S2d, but their decomposition behavior was different. For example, CH₄ is the major product in 4,4′-dmbpy/KB at 600–700 K in Figure S2d, while C₂ hydrocarbons and CO₂ are dominant for 1wt%Co–4,4′-dmbpy/KB in Figure 4. These differences suggest that the decomposition processes of 4,4′-dmbpy with and without Co are not identical.

The interesting point is that the CO₂ and C₂ desorption temperature at 550–650 K in Figure 4 overlapped with the heat-treatment temperature required to exhibit the CO₂ reduction (573–673 K; Figure 2). Therefore, it could be assumed that the decomposition of 4,4′-dmbpy coordinated to Co is the key reaction to form the active site for the CO₂ reduction. The second desorption of C₂ fragments from Co–4,4′-dmbpy/KB in Figure 4 was confirmed over 750 K, at which the temperature almost corresponded to the sharp decrease in CO₂ electroreduction activity over 773 K. Thus, the deep decomposition of 4,4′-dmbpy coordinated to Co would result in the loss of electrocatalytic activity of Co–4,4′-dmbpy/KB for the CO₂ electroreduction.

2.3. Characterization of Co–4,4′-dmbpy/KB. As described above, the electrocatalysis of Co–4,4′-dmbpy/KB depends on pyrolysis temperatures. In order to clarify the effect of heat-treatment temperatures of the electrocatalyst precursor on a structure of Co surrounding, transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and extended X-ray absorption fine structure (EXAFS) measurements were performed. To obtain a significant signal of the active site, a loading of Co was increased by 3 wt %, holding the ratio of dmbpy and Co at 5. This 3wt%Co–dmbpy/KB(673K) electrocatalyst showed good performances for the CO₂ reduction to CO, as confirmed in a previous report.33

2.3.1. TEM-EDX Analysis. Figure S3 in the Supporting Information shows TEM images and energy-dispersive X-ray (EDX) analyses of the 1wt%Co–4,4′-dmbpy/KB(673K), 2wt%Co–4,4′-dmbpy/KB(673K), and 3wt%Co–4,4′-dmbpy/KB(973K) electrocatalysts. For 1wt%Co–4,4′-dmbpy/KB(673K), only the round-shaped KB support was observed; there were no particles on the KB support in Figure S3a. An EDX analysis of the 1wt%Co–4,4′-dmbpy/KB(673K) material showed that a small amount of Co was uniformly present on the KB support in Figure S3b, indicating the extremely small Co species whose size was under the resolution of high-resolution TEM. Similar TEM images were obtained for the 3wt%Co–4,4′-dmbpy/KB(673K) material in Figure S3c. The morphology of Co species was changed by the heat treatment at 973 K.

Particles of ca. 8 nm were formed for the 3wt%Co–4,4′-dmbpy/KB(973K) material in Figure S3d, and its EDX analysis indicated that the particles are composed of Co. In addition, the EDX analysis of 3wt%Co–4,4′-dmbpy/KB(973K) showed that Co was also detected in the area of the KB surface where the particles were absent in Figure S3e. Therefore, we considered that Co particles and invisible Co species coexist in the 3wt%Co–4,4′-dmbpy/KB(973K) material. The morphological change of Co from 673 to 973 K was simply recognized as a result of sintering of Co species on the KB support.

In addition, SEM-EDS mappings with a low resolution are indicated in Figure S4a–c. The contrasts of Co and N were not good; however, Co and N elements were uniformly distributed on the surface of carbon.

2.3.2. XRD Analysis. Figure 5 shows XRD patterns of the KB support and 3wt%Co–4,4′-dmbpy/KB(343K), 3wt%Co–4,4′-dmbpy/KB(673K), and 3wt%Co–4,4′-dmbpy/KB(973K) materials. The KB showed broad diffraction lines assigned to the graphite structure in the spectrum (Figure 5a). For the 3wt%Co–4,4′-dmbpy/KB(343K), numerous diffraction lines at 10°–40° would be assigned to the Co(4,4′-dmbpy) complex in the spectrum (Figure 5b). The numerous diffraction lines disappear, and new diffraction lines assigned to CoO was faintly observed for the 3wt%Co–4,4′-dmbpy/KB(673K) material in the spectrum (Figure 5c). The crystal size of CoO on the KB support was estimated as a few nanometers. This was not in conflict with the corresponding TEM image in Figure S3c. In the XRD pattern of the 3wt%Co–4,4′-dmbpy/KB(973K) material, new diffraction lines assigned to metallic Co was observed in the spectrum (Figure 5d), corresponding to the TEM image in Figure S3d. On the other hand, changes in the carbon structure were observed in the XRD data. The diffraction line of C(002) at 23.8° of the KB in the spectrum (Figure S3a) was shifted to a higher angle in Figure S3c,d. Ozkan et al. reported that the formation of the C–N structure brought a shift to a higher angle in C(200).35 This proposed a partial formation of the C–N structure in the Co–4,4′-dmbpy/KB(673, 973K) materials.

Based on the above results, the outline of structural changes in the 3wt%Co–4,4′-dmbpy/KB materials during heat treatments could be illustrated as follows: a crystal compound of Co–4,4′-dmbpy on KB was pyrolyzed to invisible Co species in the TEM images and also CoO species at 673 K. A deep pyrolysis of the invisible Co species at 973 K resulted in the formation of Co⁰ particles; meanwhile, the invisible Co species remained on KB.

2.3.3. XPS Analysis. Figure 5i shows C1s XPS spectra of 3wt% Co–4,4′-dmbpy/KB((a) 343K, (b) 673K, and (c) 973K) and (d) KB. The spectra in Figure 5a should reflect the two components: (comp-1) a carbon structure of the KB (mainly sp³ carbon) around 286.0 eV and (comp-2) hydrogenated moieties in 4,4′-dmbpy on the KB surface around 285.5 eV. As the heat-treatment temperature became higher, the intensity of the...
became dominant. This reflected the thermal decomposition of 4,4′-dmbpy corresponding to the results of TPD-MS in Figure 4 and XRD in Figure S5.

Figure 5 shows N1s XPS spectra of the three samples. The N1s spectrum of the 3wt%Co-4,4′-dmbpy/KB(343K) material could be fitted by three components having the peaks at 398.9, 400.3, and 407.2 eV. The peaks at 398.9 and 407.2 eV were assigned to pyridinic nitrogen and nitrate from Co(NO$_3$)$_2$·6H$_2$O, respectively. The peak at 400.3 eV would be assigned to a Co–N center in the Co(4,4′-dmbpy)$_3$ complex; however, to our knowledge, the XPS spectra of Co–pyridine complexes have not been reported. As similar structures to a Co–N center, N1s binding energies of Ge and pyridinic nitrogen were observed. The previous reports suggested that the coordination of other elements to pyridine resulted in the positive shift of N1s binding energy to compare with a 398.9 eV of pyridine, which suggested the assignment of the 400.3 eV peak to Co–N bonds.

For the N1s spectrum of the 3wt%Co-4,4′-dmbpy/KB(673K) sample in Figure Sii, the peak of NO$_3$ disappeared owing to the thermal decomposition, as described in the TPD-MS profile. The peaks assigned to Co–N and pyridinic nitrogen species were observed. For the 3wt%Co-4,4′-dmbpy/KB(973K) sample, peaks assigned to Co–N, pyridinic nitrogen, graphitic nitrogen (401.5 eV) species, and nitrogen bonded to oxygen (403.8 eV) were observed.

The decrease in the intensity of the peak assigned to Co–N with the heat-treatment temperature implied that Co–N bonds were dissociated during the heat treatment, corresponding to the results of the TPD-MS and XRD studies. The observation of the peak assigned to graphitic nitrogen indicated that nitrogen atoms were incorporated in the carbon structure of the KB support at 973 K.

Figure Siii shows Co2p$_{3/2}$ XPS spectra of 3wt%Co-4,4′-dmbpy/KB(343, 673, and 973K). The Co(4,4′-dmbpy)$_3$ complex was on the KB surface of the 3wt%Co-4,4′-dmbpy/KB(343K) material. Fulghum et al. measured Co2p$_{3/2}$ XPS spectra of Co porphyrin and assigned several peaks to the Co–N center at 779–785 eV. Even though the coordination environments of Co by porphyrin and 4,4′-dmbpy are not identical, the XPS spectrum around 782 eV (779–785 eV) in Figure Siii should be assigned to the Co–N center of the Co(4,4′-dmbpy)$_3$ complex. The peak around 782 eV became weaker and a broad tail appeared at a lower binding energy with increasing heat-treatment temperature. This indicated the dissociation of Co–N bonds and formation of Co compounds in 3wt%Co-4,4′-dmbpy/KB(673 and 973K).

It was reported that Co2p$_{3/2}$ XPS spectra contributed with CoO and Co species were observed at 780.0 and 778.1 eV, respectively. It seems that a CoO compound formed on 3wt%Co-4,4′-dmbpy/KB(673K) and CoO and Co compounds formed on 3wt%Co-4,4′-dmbpy/KB(973K), which corresponded to the XRD patterns at Figure S5b,c, respectively. The XRD, TEM, and XPS data indicated that Co metal particles formed by the decomposition and reduction of the Co(4,4′-dmbpy)$_3$ complex with carbon and a part of Co metal were oxidized in air during the characterization procedures.
which is a characteristic peak of the Co–N₄ structure with D₄h symmetry. A broad shoulder peak appears at 7710 eV, which corresponds to the Co metal structure (Co foil reference). This shoulder peak was reduced by washing with HNO₃ aq., the peak at 2.2 Å disappeared. A peak at 1.8 Å was observed for the Co foil KB(673K) sample. These were assigned to the first neighboring atom of N of the dmbpy ligand. In the case of the Co–dmbpy/KB(673K) sample, a peak at 1.8 Å could be assigned to the first neighboring atom of Co. When the Co–dmbpy/KB(673K–HNO₃) sample was washed with HNO₃ aq., the peak at 2.2 Å disappeared. A peak at 1.8 Å was observed for the Co–dmbpy/KB(673K–HNO₃) sample, which is assigned to the coordination of C, N, and/or O. 

Though it is difficult to determine the coordination element, it should be assigned to the first neighboring atom of N derived from the dmbpy ligand considering the XPS results. Table 1 shows coordination numbers and distances of Co to neighboring atoms calculated from the curve-fitting results in Figure 5b. 

Table 1. Coordination Numbers and Distances of Co to Neighboring Atoms Calculated from the Curve-Fitting Results in Figure 5b

| Co–dmbpy/KB | Co– numb. | R (Å) | dE | DW |
|-------------|-----------|-------|----|----|
| not treated | N         | 2.32  | 1.90 | -9.89 | 0.046 |
| 673-treated | N         | 2.37  | 1.89 | -13.97 | 0.071 |
| 673K-HNO₃-treated | N | 3.75  | 2.09 | -2.25 | 0.085 |

The coordination structure of Co and N indicated as Co–N₄ in the Co–dmbpy/KB(673K–HNO₃) would be similar to the structures of Co–Pc and Co–TPP but not the same. 

2.4. H⁺ and CO₂ Reaction on the Active Site. Figure 7 shows the effects of partial pressure of CO₂, abbreviated P(CO₂) in CO₂, on the electroreduction of CO₂ over the 4,4′-dmbpy/KB(673K) electrocatalyst. The P(CO₂) at cathode was controlled by mixing CO₂ and Ar by mass-flow valves, and the total flow rates were fixed at 20 mL min⁻¹. The FR(CO) increased with increasing P(CO₂). The j and CE(CO₂) gradually increased with increasing P(CO₂) than 0.25 atm. On the other hand, the FR(H₂) was almost constant between 0.25 atm of P(CO₂), whereas the FR(H₂) was very high at P(CO₂) = 0 atm. The FR(H₂) should steeply increase between 0.25 and 0.25 atm of P(CO₂). 

The dependency of FR(CO), FR(H₂), CE(CO), and CE(H₂) on P(CO₂) indicates that the adsorption process of CO₂ on the cathode contributes to the rate-determining step of the electroreduction of CO₂. Apparently, the CO₂ adsorption seemed to suppress the formation of H₂ even at a low P(CO₂). Figure S4 shows the j values in streams of Ar and CO₂ at the Co–4,4′-dmbpy/KB(673K) electrocatalyst as functions of cathode potentials. The j in Ar is for the formation of H₂ abbreviated j(H₂) in Ar". The j in CO₂ is the formation of CO and H₂; therefore, the j in CO₂ is divided into j for the CO formation, j(CO) in CO₂, and for the H₂ formation, j(H₂) in
electron reduction \((z = 1)\) was the rate-determining step for the CO formation, the \(\alpha\) value was 0.23. The interpretation of lower \(\alpha\) values was discussed in the next section.

**2.5. Reaction Scheme on the Co–4,4′-dmbpy/KB Cathode.** Based on the results of the characterization studies, the structural change in Co–4,4′-dmbpy/KB during the heat treatment is proposed as shown in Figure 9. The Co–4,4′-

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**Figure 7.** Effects of \(P(CO_2)\) on (a) formation rates of CO and \(H_2\) and (b) current density and current efficiency to CO and \(H_2\) during the electroreduction of \(CO_2\) at the Co–4,4′-dmbpy/KB(673K) electrocatalyst. \(T = 273\) K, cathode catalyst: 1.0wt%Co–4,4′-dmbpy/KB(673K), cathode potential: \(-0.70\) V (SHE), gas mixture of \(CO_2\) and Ar (total 10 mL min\(^{-1}\)), other conditions same as in Figure 2.

**Figure 8.** Effects of the cathode potential on \(j\) in \(CO_2\), \(j(H_2)\) in Ar and \(CO_2\) and \(j(CO)\) in \(CO_2\). \(T = 273\) K, cathode catalyst: 1.0wt%Co–4,4′-dmbpy/KB(673K), cathode potential: \(-0.55\) to \(-0.75\) V (SHE), cathode gas (10 mL min\(^{-1}\)): \(CO_2\) or Ar, other conditions same as in Figure 1.

**Figure 9.** Reaction scheme for (a) conversion of Co–4,4′-dmbpy to the active site of Co–N\(_x\)–C\(_y\) on the KB surface, (b) electroreduction of \(H^+\) to \(H_2\) formation on the active site, and (c) electroreduction of \(CO_2\) to CO on the active site.
however, a formula and structure of $C_\text{N}_x$ indicated by hashed lines in Figure 9 had not been clarified.

Though the electrolysis conditions such as reaction phase, supporting electrolyte, pH value, etc., were very different from our conditions, it has been already reported that the Co$-\text{N}_x$ center in Co$-\text{TPP}$ and Co$-\text{Pc}$ was effective for the CO$_2$ reduction.$^{21,23,29,39,46-50}$ We have also reported that Co$-$phthalocyanine supported on a carbon support (vapor-grown carbon fiber, Showa Denko Co.) showed a lower electrocatalytic activity for the reduction of CO$_2$ to CO in the gas phase.$^{50}$. These facts proposed that a Co$-\text{N}_x$ structure was effective for the CO$_2$ reduction. However, a 2.09 Å length of Co$-\text{N}$ bonds of the Co$-\text{N}_x-\text{C}_y$ structure observed in the Co$-4,4'$-dmbpy/KB(673K) is longer than a 1.92 Å length of Co$-\text{TPP}$ and Co$-\text{Pc}$, as described in Table 1.$^{57}$ The particular structure of Co$-\text{N}_x-\text{C}_y$ would be suitable for the selective reduction of CO$_2$ to CO.

As described in the previous section, the charge transfer coefficient, $\alpha$ value, of 0.37 for $j(H_2$) in Ar was smaller than the typical value of 0.5 observed for the H$_2$ formation on the conventional Pt electrode. If the active site for the electrode-reduction of H$^+$ is the Co$-\text{N}_x-\text{C}_y$ site, then the Co$-\text{N}_x-\text{C}_y$ site is isolated on the KB surface, as described in the XAFS study. Atomic hydrogen species on the Co$-\text{N}_x-\text{C}_y$ site should migrate to the other atomic hydrogen species and coupled to H$_2$, as indicated in Figure 9b.

Therefore, the migration process of atomic hydrogen species should affect the j value (FR(H$_2$)). The $\alpha$ value of 0.23 for the $j(j(H_2$) in CO$_2$) was about a half of that of $j(H_2$) in Ar. This indicates that the H$_2$ formation on the Co$-4,4'$-dmbpy/KB(673K) electrocatalyst was remarkably inhibited in CO$_2$. We propose from this fact that the adsorption of CO$_2$ on the electrocatalyst surface inhibits the migration of atomic hydrogen species and decelerates the H$_2$ formation. The $\alpha$ value of 0.23 for the CO formation was also small. The electrochemical reduction was slow, and the chemical reaction affected the rate-determining step in the CO formation. We propose from this fact that atomic hydrogen species on the Co$-\text{N}_x-\text{C}_y$ site react with the adsorbed CO$_2$ on the surface. This chemical reaction should be slow, and the adducts of hydrogen species and CO$_2$ on the Co$-\text{N}_x-\text{C}_y$ site finally produce CO, as shown in Figure 9c.

As described in Section 1, Strasser’s group reported the active Ni$-\text{N}_x$ electrocatalyst for the reduction of CO$_2$ to CO using carbonate and KOH solutions and identified the active site of the Ni$-\text{N}_x$ structure; however, the Ni and other metal electrocatalysts did not work for the reduction of CO$_2$ but remarkably promoted H$_2$ formation in acidic conditions at pH < 1.$^{29,30}$ Strasser’s group Ni$-\text{N}_x$ structure and our Co$-\text{N}_x$ structure are very similar; however, our Co$-\text{N}_x$ electrocatalyst was very active and stable (Figure S1) for the CO$_2$ reduction under strong acidic conditions of Nafton-H at pH < 0. This fact suggests that the fine structure is different.

As described in Figures 2 and 3, the Co$-6,6'$-dabpy/KB precursor was activated at a lower temperature of 473 K and showed maxima FR(CO) and CE(CO) by the 573 K treatment. We could not reveal the activation process of the Co$-6,6'$-dabpy/KB precursor and a structure of active site on the Co$-6,6'$-dabpy/KB(573K) electrocatalyst. It is interesting that the active structures of the two electrocatalysts are the same or not. By the way, we have studied the direct synthesis H$_2$O$_2$ by the electroreduction of O$_2$ at the Co$-\text{bipyridine}$, phenanthroline, and porphyrin derivatives supported on carbons heat-treated around 1023 K.$^{29,51-54}$ Recently, the synthesis of a high concentration of pure H$_2$O$_2$ aqueous solutions with 18.7 wt % (5.5 M) was achieved by using an electrocatalyst prepared from Co$-\text{TPP}$/KB pyrolyzed at 1023 K.$^{54}$ The structure of the active site was identified as Co bicoordinated with N on the carbon surface, abbreviated Co$-\text{N}_x$ structure, by characterization studies using EXAFS, XPS, etc.$^{51-53}$ Although the initial Co loading of 0.05 wt % for the Co$-\text{N}_x$ electrocatalyst is far from that of 1.0 wt % for the Co$-4,4'$-dmbpy/KB(673K) electrocatalyst, the Co$-\text{N}_x$ electrocatalyst did not show electrocatalytic activity for the CO$_2$ reduction;$^{29}$ in contrast, the Co$-4,4'$-dmbpy/KB(673K) electrocatalyst, Co$-\text{N}_x$, was not active for the H$_2$O$_2$ formation. The two active sites consist of the same elements (Co, N, and C), but they perform different and unique electrocatalysis, respectively. We will report details in electrocatalysis depending on $y$ in Co$-\text{N}_x-\text{C}_y$ compounds prepared from Co$-4,4'$-dmbpy/KB, Co$-6,6'$-dabpy/KB, and Co$-\text{TPP}$/KB precursors.

3. CONCLUSIONS

Electroreduction of CO$_2$ to CO using the gas-electrolysis cell with the Nafton-H membrane electrolyte (strong acidic conditions) and electrocatalysts prepared by pyrolysis of N-bidentate ligands, Co(NO$_3$)$_2$, and KB was studied. Pyrolysis temperatures remarkably affected their electrocatalytic activities. The Co$-4,4'$-dmbpy/KB(673K) electrocatalyst showed the highest performance for the CO$_2$ reduction to CO among the electrocatalysts tested in this work. The Co$-\text{N}_x$ structure was identified as the active site for the reduction of CO$_2$ to CO from the characterization studies using EXAFS, XPS, TEM-EDX, XRD, and TPD-MS. The Co$-\text{N}_x$ structure resembled Co$-\text{TPP}$ and Co$-\text{Pc}$, but the distance of the Co$-\text{N}$ bonds was longer than those of Co$-\text{TPP}$ and Co$-\text{Pc}$. This unique structure would be suitable for the reduction of CO$_2$. How to synthesize the Co$-\text{N}_x$ active site with a higher concentration on the GDE is essential to realize an actual CO$_2$ reduction process. The onset potential for the CO formation on the Co$-4,4'$-dmbpy/KB(673K) electrocatalyst was about −0.50 V (SHE), which was fairly positive than other studies;$^{21-26,47-48}$ however, we have to improve the electrocatalysis and the onset potential near −0.11 V (eq 1) and to achieve a significant j value, for example, 100 mA cm$^{-2}$, with a higher CE(CO) under strong acidic conditions to contribute a solution for the global warming problem.

4. EXPERIMENTAL SECTION

4.1. Electro catalyst Preparation. N-bidentate ligands used in this study were 2,2'-bipyridine (1: bpy), 4,4'-dimethyl-2,2'-bipyridine (2: 4,4'-dmbpy), 5,5'-dimethyl-2,2'-bipyridine (3: 5,5'-dmbpy), 6,6'-dimethyl-2,2'-bipyridine (4: 6,6'-dmbpy), 6,6'-diamo-2,2'-bipyrin (5: 6,6'-dabpy), 4,4'-di-tert-butyl-2,2'-bipyridine (6: 4,4'-dtBupy), and 1,10-phenanthroline (7: phen). A ligand and Co(NO$_3$)$_2$$\cdot$6H$_2$O with a ratio of 5 (mol/mol) were stirred in ethanol to form Co complexes. Ketjenblack EC300J powder (KB; 790 m$^2$ g$^{-1}$) was added in the solutions of Co complexes and mixed well using a magnetic stir bar. Electro catalyst precursors were prepared by drying the ethanol solvent in the mixture. The precursor powder was placed in a flat-bottom quartz reactor and was activated by the heat treatment in a He stream for 1 h at 423−973 K for 3 h. A loading of Co was 1.00 wt %.

When we used N$_2$ or Ar instead of He during the catalytic synthesis, very good reproducibility of catalytic activities was obtained. We monitored desorbed products such as CO, CO$_2$,
H₂O, N₂, N₂O, CH₄, and light hydrocarbons from the catalyst precursors by TCD chromatography with He carrier gas. Therefore, we used He during the catalyst synthesis.

4.2. Cathode and Anode Preparation. A round cathode sheet (0.1 mm-thick, 2 cm²) was prepared by the hot-pressing method using the prepared 1wt%Co(N-ligand)/KB electrocatalyst (18 mg), vapor-grown carbon fiber (VGCF; Showa Denko Co., 30 mg), and PTFE powder (F-104, Daikin Co.; 3 mg). A content of Co in a sheet of the cathode was 0.18 mg (3.05 μmol). A loading of Co was 1.53 μmol cm⁻². The anode was prepared from Pt(50 wt %)/KB (25 mg), VGCF (25 mg), and the PTFE powder (5 mg) in a similar way. A loading of Pt was 32.05 μmol cm⁻².

4.3. Electrolysis Procedures. The membrane electrode assembly (MEA) was fabricated by hot-pressing the cathode, Nafion 117, and the anode under 59 MPa at 413 K. An electrolysis cell of diaphragm type was assembled using the MEA, glass flange parts, and PTFE parts, as indicated in Figure 1. Ar (20 mL min⁻¹) was flowed through the cell to purge air and then pure H₂ (20 mL min⁻¹) and pure CO₂ (10 mL min⁻¹) were introduced into the anode and cathode compartments, respectively. In addition, to humidify the Nafion membrane, H₂ was bubbled through deionized water at 273 K and the relative humidity was about 80%. Electrochemical reduction was performed under potentiostatic conditions using an electrochemical measurement system (Hokuto Denko Co. HZ-5000) and a Ag/AgCl reference electrode (0.197 V vs SHE) at 273 K. Potentials in this paper were converted to those based on the SHE.

When we replaced the anode reaction from H₂ oxidation to water oxidation, total voltages between the cathode and anode increased but the same electroreduction of CO₂ at the Co(N-ligand)/KB cathode occurred. To focus on the cathode reaction and the electrocatalysis, we employed a fast anode reaction of H₂ oxidation. In addition, the anode reaction using H₂ can function as an apparent reversible hydrogen electrode (RHE). We utilized the apparent RHE to evaluate the reliability of the cathode potentials.

4.4. Product Analysis. After applying each cathode potential from −0.5 to −0.75 V (SHE) for 30 min, we observed steady states of the electroreduction of CO₂. A reaction gas mixture from the cathode was analyzed three times for every 10 min using an online six-way valve connected to a gas chromatograph (CO analysis: Shimadzu GC-8AP1 with a TCD detector, a 5 Å molecular sieves column, and He carrier gas) and using a sampling port and a gas-tight microsyringe (H₂ analysis: Shimadzu GC-8AP1 with a TCD detector, an activated-carbon column, and Ar carrier gas). Product yields were calculated from gas chromatography data and calibration factors. Formation rates (FR) of CO and H₂ were calculated from the yields and outlet flow rates. Current efficiencies (CE) to CO and H₂ were evaluated from (eq 5):

\[ CE = \frac{\text{charge for product yields}}{\text{sum of charge passed}} \times 100\% \]  

(5)

4.5. TPD-MS Measurements. Temperature-programmed desorption mass spectrometry measurements were performed by combining a catalyst analyzer (BELCAT-B, MicrotracBEL Corp.) and a gas analytical system equipped with quadrupole mass spectrometer (M-200GA-DM, Anelva Corp.). The sample powder was placed in a quartz tube and attached to the catalyst analyzer. The sample was heated to 423 K at 10 K min⁻¹ and held for 1 h, and subsequently the temperature was raised to 1223 K at 4 K min⁻¹. The measurement was conducted in a He gas stream of 20 mL min⁻¹. A part of the outlet gas was introduced into the gas analytical system by using a capillary tube to obtain the TPD-MS profile.

4.6. TEM and SEM Observation. Transmission electron microscopy images were measured using a JEM-2010F (JEOL) microscope equipped with an energy-dispersive X-ray spectrometry instrument (Genesis). Scanning electron microscopy images were measured using a JCM-6000Plus (JEOL).

4.7. XRD Analysis. X-ray diffraction patterns were measured using a MiniFlex 600/TTSS (Rigaku) diffractometer using Cu Kα X-ray (1.5418 Å).

4.8. XPS Measurements. X-ray photoelectron spectroscopy measurements were carried out using a JPS-9010MC (JEOL) equipped with a monochromatic Al Kα source operated at 25 kV and 10 mA. A C1s binding energy of 284.6 eV was used for the charge collection. Background spectra were subtracted by the Shirley method. N1s spectra were curve-fitted using Lorentzian–Gaussian combination peaks.

4.9. XAFS Measurement. XAFS spectra of Co K-edge were measured by transmission mode at the beamline BL9C of Photon Factory (PF) of the Institute for Materials Structures Science, High Energy Accelerator Research Organization (KEK-IMSS), Tsukuba, Japan. The X-ray beam was monochromatized using a Si(111) double-crystal monochromator. The X-ray energy was calibrated using Co⁶ foil (E = 7709 eV). XAFS samples were prepared by mixing the electrocatalyst and BN powders and pressing into a pellet (10 mm in diameter). The X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were analyzed using the REX2000 software (Rigaku). The backscattering amplitudes and the phase shifts were calculated using the FEFF program by setting S02 to 1.0 without SCF calculations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01510.

(Figure S1) Time courses of the reduction, (Figure S2) additional TPD-Mass data, (Figure S3) TEM-EDX images of Co-dmbpy/KB materials, (Figure S4) SEM-EDS mapping, (Figure S5) XRD patterns of Co-dmbpy/KB materials, and (Figure S6), j-potential data for CO and H₂ formations (PDF)

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Notes
The authors declare no competing financial interest.

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