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Characterization of a Rh(III) porphyrin–CO complex: its structure and reactivity with an electron acceptor†

Shin-ichi Yamazaki,*[a] Masaru Yao,[a] Masafumi Asahi,[a] Hiroyasu Sato,[b] Akihito Yamano[b] and Tsutomu Ioroi[a]

To analyse the electrocatalytic oxidation of carbon monoxide by Rh porphyrins, we isolated a CO-adduct of Rh octaethylporphyrin, and examined its properties and reactivity by IR, NMR, and X-ray crystallographic analyses. The results indicate that the CO adduct of Rh octaethylporphyrin is vulnerable to nucleophilic attack by H_2O. The CO-adduct was easily oxidized by an electron acceptor (1,4-naphthoquinone) to generate CO_2. This indicates that CO is sufficiently activated in the CO complex of Rh octaethylporphyrin to reduce an electron acceptor. This mechanism is in contrast to that for the CO oxidation by Pt-based electrocatalysts.

In the improvement of stationary polymer electrolyte fuel cells (PEFCs), the development of CO-tolerant anode catalysts is very important, since Pt-based anode catalysts are strongly poisoned by a small amount of CO, which is contained in the anode gas.[1] To date, a wide variety of CO-tolerant anode catalysts have been developed.[2] Pt–Ru catalysts, which interact very little with CO, are currently used as CO-tolerant anode catalysts. However, even with state-of-the-art Pt–Ru catalysts, PEFCs are still vulnerable to high concentrations of CO (>500 ppm).

The electrochemical oxidation of CO is a key reaction for the development of such anode catalysts, since this reaction can decrease the CO concentration in an anode catalyst. However, current Pt–Ru catalysts require high overpotentials for the CO oxidation and hence the reaction hardly occurs at the anode potentials in PEFCs (<0.1 V). Catalysts that promote the CO oxidation at low overpotentials should help enhance CO-tolerance.

For this purpose, we turned our attention to Rh porphyrin catalysts. It has been demonstrated that Rh porphyrins can catalyze CO at low overpotentials.[3,4] We have shown that Rh porphyrins with hydrophilic groups (carboxy and sulfo groups) exhibit better activity, and catalyze the CO oxidation at much lower overpotentials than Pt–Ru catalysts.[4b–d] State-of-the-art Rh porphyrin catalysts can oxidize CO below 0.1 V *vs.* a reversible hydrogen electrode (RHE).[4c] A combined catalyst of a Rh porphyrin and a Pt–Ru catalyst tolerates a high concentration of CO better than a Pt–Ru catalyst alone.[4d] A PEFC that uses a Rh porphyrin as an anode catalyst delivered high power ($95\ \mathrm{mA\ cm^{-2}}$, $44\ \mathrm{mW\ cm^{-2}}$) when CO was supplied as a fuel.[4a] This high current means that Rh porphyrins can be used in the severe environments of PEFCs.

Compared to a lot of findings on the catalytic activity and application of Rh porphyrins, the information on the reaction pathway of the CO electro-oxidation is not abundant. Hendriksen *et al.* proposed a mechanism of $[\mathrm{RhCl_2(CO)_2}]^-$-catalyzed CO oxidation by NO. They showed that the coordinated CO participates in the catalytic reaction.[5] With regard to the (electro) catalytic CO oxidation by Rh porphyrins, it has been postulated that CO is coordinated to a Rh porphyrin.[4b,6] The CO complex is believed to react with water to generate a carboxy intermediate, which in turn may give electrons to an electron acceptor to afford CO-free Rh porphyrin and CO_2. Also in CO electro-oxidation by Co porphyrin, a similar mechanism may be presented.[7]

Thus, the $\mathrm{Rh^{III}}$ porphyrin–CO complex is supposed to be an important intermediate for catalytic CO oxidation. This complex was reported more than 40 years ago.[8] The IR and UV spectra of CO coordinated to $\mathrm{Rh^{III}}$ porphyrins were examined.[8–10] ^{1}H-NMR was also measured with a CO complex with $\mathrm{Rh^{III}(OEP)(Cl)}$.[10a] However, more information on the properties of the $\mathrm{Rh^{III}}$ porphyrin–CO complex is not available, while metalloradical CO complexes of $\mathrm{Rh^{II}}$ porphyrin[11] and $\mathrm{Rh^{I}}$ carbonyl complexes[12] have been intensively investigated.

We are also interested in the reactivity of the $\mathrm{Rh^{III}}$ porphyrin–CO complex. Although the reactivities of the CO adduct with alkoxide[8b,9] and CO in the presence of KOH[13] were exam-

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[a] *Research Institute of Electrochemical Energy, Department of Energy and Environment, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31, Midorigaoka, Ikeda, Osaka 563-8577, Japan. E-mail: s-yamazaki@aist.go.jp; Fax: +81-72-751-9629; Tel: +81-72-751-9653*

[b] *Rigaku Corporation, 3-9-12 Matubara, Akishima, Tokyo 196-8666, Japan*

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ined, the reactivity of the complex with an electron acceptor has not been examined. The reactivity with an electron acceptor would be significant for elucidating the (electro)catalytic CO oxidation.

From these backgrounds, we tried to examine the properties of a Rh^{III} porphyrin–CO complex, and investigated the reactivity of the complex toward an electron acceptor. In this work, a Rh^{III} porphyrin–CO complex was characterized by X-ray crystallography, NMR, and IR. We also examined the reactivity of the CO complex with an electron acceptor (1,4-naphthoquinone (NQ)).

Rh^{III} octaethylporphyrin chloride ([Rh^{III}(OEP)(Cl)], Chart 1) was synthesized as described in the literature (see the ESI†).[14] ^{13}CO (^{13}C, 99%) was purchased from Cambridge Isotope Laboratories, Inc. NQ was purchased from Tokyo Kasei Corp. Other regents were obtained commercially, and used as received.

First, we analysed the reaction between [Rh^{III}(OEP)(Cl)] and CO in CH_2Cl_2 with UV (Fig. S1†). On introduction of CO, the spectrum of [Rh^{III}(OEP)(Cl)] underwent red shift, indicating that [Rh^{III}(OEP)(Cl)] reacts with CO in CH_2Cl_2. Similar spectral shifts have been reported in the literature.[9,10a,c]

The product of the reaction between [Rh^{III}(OEP)(Cl)] and CO was subjected to X-ray crystallographic analysis. The result (Fig. 1) clearly shows that [Rh^{III}(OEP)(CO)(Cl)] (Chart 1) is generated from the reaction between [Rh^{III}(OEP)(Cl)] and CO. CO and Cl coordinate to the Rh atom as axial ligands. There is no anion other than Cl$^-$ in the crystal of [Rh^{III}(OEP)(CO)(Cl)]; this indicates that Rh is trivalent. The distances and the angle of Rh–C–O strongly suggest that CO coordinates to Rh *via* the C atom. This near-linearity of Rh–C–O (173.4(12)°) is typical of carbon monoxide. This is in contrast to the bent structure of Rh–C–O in Rh(OEP)–CHO (129.6(5)°).[15] In [Rh^{III}(OEP)(CO)(Cl)], the axial ligands (Cl and CO) occupy equivalent symmetrical positions at the same probability. Therefore, the detailed bond distances of Rh–C and C–O remain unclear due to the existence of Cl. It is very difficult to discuss the electronic state of CO coordinated to Rh only from the results of the X-ray crystallographic analysis. Then, we analysed the complex with ^{13}C-NMR and IR.

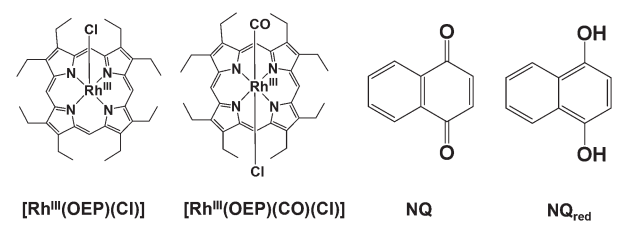

Chart 1 Chemical structures of the compounds used in this study.

For the analysis of NMR, ^{13}CO was introduced into [Rh^{III}(OEP)(Cl)] in a $CDCl_3$ solution. The ^{13}C-NMR spectrum was recorded after the reaction, and the result is shown in Fig. 2 (δ 160.2(d, J = 58.9 Hz), 143.1, 139.2, 98.1, 20.1, 18.5 ppm). The introduction of ^{13}CO generated a split peak at 160.2 ppm. This signal is reasonably ascribed to a CO molecule coordinated to the Rh octaethylporphyrin. The coupling constant of 58.9 Hz is similar to the values reported for Rh–C bonds.[16,17] This indicates that CO is coordinated to Rh through the C atom, supporting the results of crystallographic analysis. A dimer of Rh(OEP) ([Rh(OEP)]$_2$) has been reported to react with CO to generate [Rh(OEP)]$_2$–CO, Rh(OEP)–CO–Rh(OEP), or Rh(OEP)–CO–CO–Rh(OEP).[16] However, the ^{13}C-NMR signals of the terminal CO in [Rh(OEP)]$_2$–CO were not observed due to the quick exchange of CO with dissolved CO. In contrast, the terminal CO in [Rh^{III}(OEP)(CO)(Cl)] exhibited strong peaks at δ 160.2, which indicates that the terminal CO does not dissociate in $CDCl_3$ within the NMR timescale.

We also examined the IR spectra of [Rh^{III}(OEP)(CO)(Cl)] and [Rh^{III}(OEP)(^{13}CO)(Cl)]. IR analyses of the complex between Rh porphyrins and CO have already been conducted by several researchers including our group.[4b,8,9,10a] Also with regard to the complex between [Rh^{III}(OEP)(Cl)] and CO, an IR analysis was conducted by Thackray *et al.*[10a] The IR spectrum of this crystalline powder is shown in Fig. S2.† The peak (2086 cm^{-1}) coincides with the reported value for a Rh-OEP and CO complex.[10a] When ^{13}CO was used, the peak underwent a shift toward a lower wavenumber (2039 cm^{-1}). The observed isotopic shift (47 cm^{-1}) is very close to the value (45 cm^{-1})

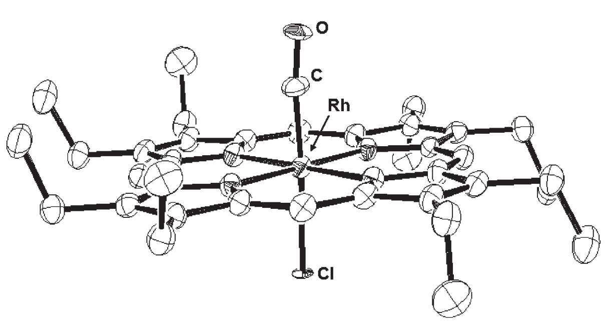

Fig. 1 X-ray crystallographic structure of [Rh^{III}(OEP)(CO)(Cl)] with 50% probability ellipsoids. Hydrogen atoms and an uncoordinated solvent molecule are omitted for clarity.

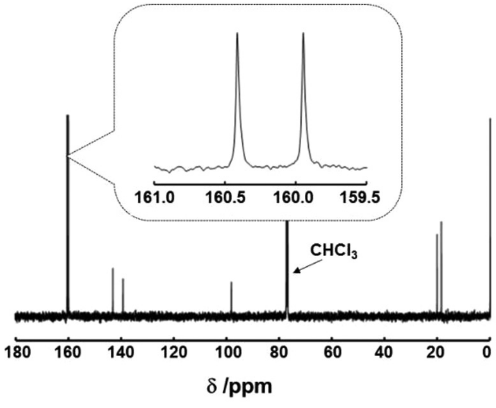

Fig. 2 A ^{13}C-NMR spectrum of [Rh^{III}(OEP)(Cl)(^{13}CO)] in $CDCl_3$.

obtained by the harmonic oscillator approximation of the C–O stretching bond.[18] This also supports that the peak is derived from CO. The wavenumber of CO in [Rh^{III}(OEP)(CO)(Cl)] is much higher than those of CO-complexes of metalloporphyrins such as Fe porphyrins.[18] This indicates that π back-donation from Rh to CO is very weak compared to those for other metals.[19] Weak π back-donation is also observed in a formyl complex of Rh porphyrin.[15]

Anson *et al.* analysed electrochemical CO oxidation by Co octaethylporphyrin, and postulated that CO coordinates to Co *via* σ-donation from C to Co in the reaction.[7] Our results strongly suggest that the contribution of π-back-donation to the CO–Rh bond is small. This situation should decrease the electron density on the C atom, and hence the C atom will be vulnerable to nucleophilic attack by H_2O. NMR spectra indicate that [Rh^{III}(OEP)(CO)(Cl)] is stable from kinetic viewpoints, but the coordinated CO is considered to be activated for CO oxidation.

Overall, the results indicate that CO coordinates to [Rh^{III}(OEP)(Cl)] to form [Rh^{III}(OEP)(CO)(Cl)], and CO on the [Rh^{III}(OEP)(CO)(Cl)] would be feasible to nucleophilic attack by H_2O. However, it remains unclear whether [Rh^{III}(OEP)(CO)(Cl)] undergoes oxidation by an electron acceptor in the presence of water. Therefore, we next examined the reaction of [Rh^{III}(OEP)(CO)(Cl)] with an electron acceptor to check this possibility. We chose 1,4-naphthoquinone (NQ, Chart 1) as an electron acceptor. The reaction was analysed by ^{1}H-NMR. This electron transfer needs water, and hence a mixed solvent of acetone-d_6 (0.9 mL) and water (0.1 mL) was used for this experiment as a solvent.

NQ (4.4 μmol) gave signals at δ 8.05–8.08 (m, C–*H*), 7.90–7.94 (m, C–*H*), and 7.10 (s, C–*H*) in the mixed solvent. The reduced form of NQ (NQ$_{red}$, Chart 1), which was prepared by the H_2/Pt catalyst system, gave signals at δ 9.13 (s, O–*H*), δ 8.13–8.16 (m, C–*H*), 7.42–7.46 (m, C–*H*), and 6.74 (s, C–*H*).

On the addition of [Rh^{III}(OEP)(CO)(Cl)] (4.4 μmol) to the NQ (4.4 μmol) solution, clear peaks at δ 9.19 (s, O–*H*),[20] δ 8.13–8.16 (m, C–*H*), 7.42–7.46 (m, C–*H*), and 6.74 (s, C–*H*) emerged. These peaks can be ascribed to the reduced form of NQ (NQ$_{red}$). The peaks of NQ$_{red}$ were not observed when CO gas was passed through the solution of NQ without the Rh porphyrin. These results indicate that NQ was reduced by [Rh^{III}(OEP)(CO)(Cl)] in the presence of water. This reaction strongly suggests that a CO-adduct of a Rh porphyrin is an intermediate of (electro)catalytic CO oxidation by the Rh porphyrins. The generation of [Rh^{III}(OEP)(CO)(Cl)] and the electron transfer from [Rh^{III}(OEP)(CO)(Cl)] to NQ would be a main pathway of the CO oxidation by Rh porphyrins.

A conceivable overall catalytic reaction cycle is depicted in Fig. 3. This cycle is similar to the previously reported ones.[3,5–7] Step (A) represents the coordination of CO on [Rh^{III}(OEP)(Cl)], and steps (B) and (C) correspond the reaction between [Rh^{III}(OEP)(CO)(Cl)] and NQ. A carboxy intermediate would be involved in the reaction as reported previously.[3,5–7] The nucleophilic addition of H_2O to CO coordinated to the Rh porphyrin generates this carboxy intermediate (step (B)). NQ oxidizes the carboxy intermediate to regenerate the CO-free Rh porphyrin (step (C)). An axial ligand might change from Cl if other ligand candidates exist in the system, since Cl$^-$ is once dissociated in step (B) in the mechanism.

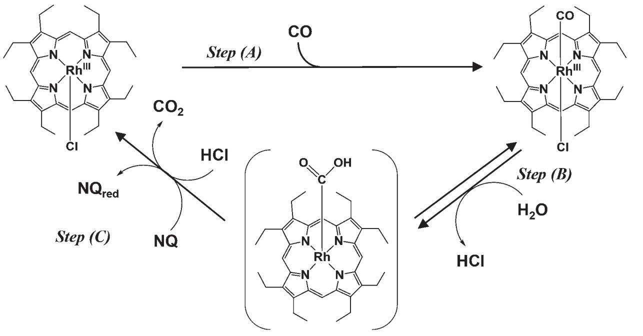

Fig. 3 A proposed reaction mechanism of catalytic CO oxidation by [Rh^{III}(OEP)(Cl)].

NQ (δ 8.05–8.08, δ 7.90–7.94, and δ 7.10) was also detected after the reaction between NQ and [Rh^{III}(OEP)(CO)(Cl)]. Even though an equivalent amount of [Rh^{III}(OEP)(CO)(Cl)] was added, NQ remained after the reaction. The ratio of peaks at δ 7.10 (NQ) and δ 6.74 (NQ$_{red}$) indicates that the amount of NQ is *ca.* 73% of the sum of NQ and NQ$_{red}$. This suggests that [Rh^{III}(OEP)(CO)(Cl)] is decomposed before the reaction with NQ in the mixed solvent containing water. A possible reason is the dissociation of CO due to the ligation of H_2O (the conversion from [Rh^{III}(OEP)(CO)(Cl)] to [Rh^{III}(OEP)(H_2O)(Cl)]) in the mixed solvent.

Finally, we examined a catalytic CO oxidation by NQ in the presence of a small amount of [Rh^{III}(OEP)(Cl)]. The reaction is denoted as follows:

$$\mathrm{CO} + \mathrm{NQ} + \mathrm{H_2O} \rightarrow \mathrm{CO_2} + \mathrm{NQ_{red}} \tag{1}$$

NQ (10 mM) was dissolved in a mixed solvent of acetone (4.5 mL) and water (0.5 mL). The solution was sealed with a rubber cap. CO was passed through this solution. [Rh^{III}(OEP)(Cl)] (0.1 mM, 0.5 μmol) was injected to the solution. The gas phase above the solution was subjected to analysis by gas chromatography after the reaction. The generation of CO_2 (50 μmol) was clearly observed 1 hour after the addition of [Rh^{III}(OEP)(Cl)].[21] This result indicates that [Rh^{III}(OEP)(Cl)] catalyses CO oxidation by NQ (Fig. 3). A similar catalytic oxidation (CO oxidation by indigo carmine) has already been realized in aqueous solution using a water-soluble Rh porphyrin.[6]

The possible pathway of CO oxidation by Rh porphyrin (CO activation and the reaction between the CO-adduct and an electron acceptor) is totally different from that for CO oxidation by Pt-based electrocatalysts.[2a–c] A water molecule is supposed to be activated for the oxidation of CO by Pt catalysts. In contrast, in the CO oxidation of a Rh porphyrin, CO is activated with the coordination on the Rh atom. The activation of a water molecule is not necessary for the CO oxidation. This reaction mechanism would be responsible for low overpotentials for electrocatalytic CO oxidation by a Rh porphyrin, since activation of a water molecule needs large overpotentials.

Conclusions

We obtained [Rh^{III}(OEP)(CO)(Cl)] from the reaction of [Rh^{III}(OEP)(Cl)] with CO in a non-aqueous solvent (CH_2Cl_2), and analysed the CO-adduct by IR, NMR, and X-ray crystallography. The results showed that back-donation from Rh to C is relatively low among metalloporphyrin–CO complexes. This suggests that CO on the Rh porphyrin easily undergoes nucleophilic attack by H_2O. This property is correlated with the (electro)catalytic oxidation of CO by Rh porphyrins. Actually, [Rh^{III}(OEP)(CO)(Cl)] reduced NQ, an electron acceptor, in acetone-d_6 containing water. Thus, CO is activated on a Rh porphyrin for the oxidation by an electron acceptor.

Recently, studies on Rh porphyrins as a catalyst for the oxidation of alcohols and sugars have been reported.[14,22,23] The mechanistic analysis of CO oxidation in this work might shed light on the analysis of these oxidation reactions.

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