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ELECTROCATALYTIC BEHAVIOR OF METAL PORPHYRINS IN THE REDUCTION OF CARBON DIOXIDE

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The catalytic activity of metal porphyrins for the electroreduction of carbon dioxide was investigated by the measurements of current-potential curves on the Hg(Pt) electrode in aqueous electrolytic solutions. Metal-free, cobalt, iron and copper porphyrins(mesotetracarboxyphenylporphyrins, tetraphenylporphinesulfonate) were examined. Cobalt complexes were active but other metal porphyrins showed no activity. The reduction product was confirmed to be formic acid by the resorcinol test.

In the previous paper,[1)] we reported that tetrasulfonated cobalt and nickel phthalocyanines homogeneously dissolved in aqueous solutions have catalytic activities in the reduction of CO_2, but the iron complexes showed no activity. The catalytic mechanism is not still clear and more systematic investigations are required with special reference to the molecular structure of the catalysts. In this respect we examined the electrocatalytic behavior of metal porphyrins which have the molecular structure similar to phthalocyanines.

Mesotetracarboxyphenylporphine(TCPP), tetraphenylporphinesulfonate($TPPS_3$) and their metal complexes(metal TCPP, metal $TPPS_3$) were prepared in our laboratory by the methods described in the literatures.[2),3),4),5),6),7)] Products were identified by absorption spectra which show the Soret and Q bands. Purification of CO_2, N_2 and water, and the measurements of current-potential curves were made in the same manner as in the previous paper.[1)]

In order to analyze the product resulting from the reduction of CO_2, the electrolysis was made over night under CO_2 bubbling in an electrolytic cell with a working electrode of mercury pool and a counter electrode of platinum coil. Anode and cathode compartments were separated by a glass filter. The electrolytic solutions were Clark-Lubs buffer solutions in the pH range 8.0 to 10.3 containing the cobalt complex of mesotetracarboxyphenyl porphine(CoTCPP). The cell voltage was controlled so that the electrode potential of the mercury pool was in the range of 1.1V to 1.5V vs.SCE. The solution was acidified with dilute sulfuric acid after the electrolysis, and CoTCPP was precipitated and separated with a centrifuge and filter papers. The filtrate was analyzed by the color reaction with resorcinol. Although this reaction provides a simple method for the detection of carboxylic acids,[9)] it is not applicable to the solution contanining metal $TPPS_3$'s because of their high solubility over a wide range of pH.

Figure 1 shows the typical current-potential curves obtained in the solution with CoTCPP or $CoTPPS_3$, and without catalyst. These curves were obtained by the potential sweep to the cathodic direction from -0.5 V vs.SCE at which the electrode potential was held for 20 to 30 minutes under CO_2 or N_2 bubbling. These gases were passed over the solution during the potential sweep. The current plateau at about -1.3 V decreased with successive potential sweep and reached to a steady value, and it disappeared again after CO_2 was excluded from the solution by the bubbling of N_2. The height of the current plateau slightly increased with increasing the concentration of the catalysts up to 2×10^{-4} M and reached to a constant value at higher concentrations. The addition of Na_2CO_3 or $NaHCO_3$ to the solution had no influence on the current.

These facts indicate that the current plateau at -1.3 V is due to the electroreduction of CO_2 catalyzed by CoTCPP or $CoTPPS_3$ which may form coordinated complexes with CO_2 at the electrode surface. From the current-potential curves, CoTCPP and $CoTPPS_3$ seem to show catalytic effects similar to tetrasulfonated cobalt

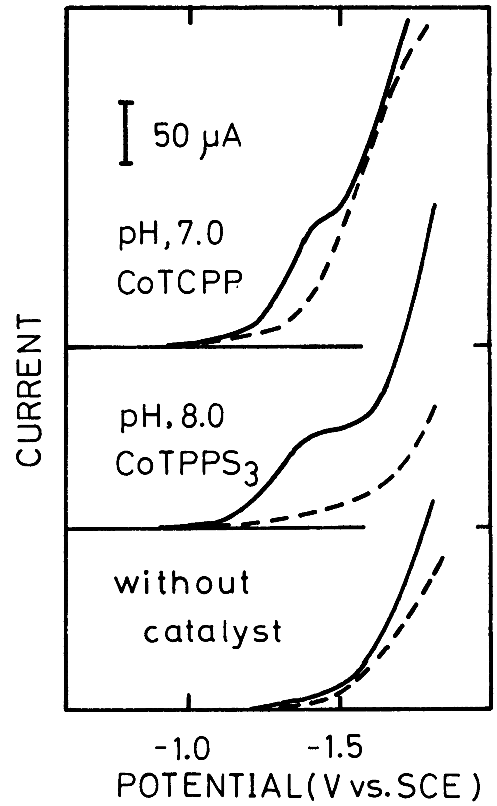

Fig.1. Effect of catalysts(5×10^{-4}M) on the cathodic current-potential curves in Clark-Lubs buffer solutions(Phosphate buffer). Solid line, CO_2 bubbling; dotted line, N_2 bubbling; sweep rate, 120 mV/s.

phthalocyanine(CoTSP), but are less active than the latter. Only cobalt complexes of the examined porphyrins showed activity, which is a little different from the results observed for metal phthalocyanines, because tetrasulfonated nickel phthalocyanine1) and iron octacarboxy phthalocyanine8) have also activities for the reduction of CO_2. Therefore, the catalytic activities seem to depend not only on the central metal ions but also on ligands. The role of the central metal ions is already studied in detail on the electroreduction of oxygen, but the discussion which takes the effects of ligands into consideration seems to be still insufficient at present. An accumulation of knowledge of the relation between the molecular structure and the catalytic activities is necessary for a clear understanding of the catalytic mechanism.

The product resulting from the reduction of CO_2 catalyzed by CoTCPP was confirmed to be formic acid but the product was not analyzed in the case of $CoTPPS_3$. As it is already known that small amounts of formic acid are also formed by the electroreduction of CO_2 on mercury at -1.1 V to -1.5 V even without catalyst,10) it is further necessary to evaluate the increased amount of formic acid by the catalysis and to investigate any other products. Such a investigation is now under way.

Conclusion

We found that CoTCPP and $CoTPPS_3$ showed catalytic activities for the reduction of CO_2 in aqueous solution. Comparing these catlysts with CoTSP, they are less active. The fact that only cobalt complexes are active in porphyrins, contrary to the results of metal phthalocyanines, indicates that the structure of the ligand also plays an important role in catalytic behavior as well as the central metal ions.

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