

SANDIA REPORT

SAND97-0414 • UC-1404

Unlimited Release

Printed February 1997

RECEIVED

APR 16 1997

OSTI

Solar Photocatalytic Conversion of CO₂ to Methanol

Gail Ryba, John Shelnut, Michael R. Prairie, Roger A. Assink

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

Approved for public release; distribution is unlimited.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED



Sandia National Laboratories

MASTER

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Prices available from (615) 576-8401, FTS 626-8401

Available to the public from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd
Springfield, VA 22161

NTIS price codes
Printed copy: A03
Microfiche copy: A01

SAND 97-0414
Unlimited Release
Printed February 1997

Distribution
Category UC-1404

SOLAR PHOTOCATALYTIC CONVERSION OF CO₂ TO METHANOL

Gail Ryba, John Shelnett, Fuel Science Department
Michael R. Prairie, Solar Thermal Test Department
Roger A. Assink, Materials Aging and Reliability: Bulk Properties Dept.
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185-0710

ABSTRACT

This report summarizes the three-year LDRD program directed at developing catalysts based on metalloporphyrins to reduce carbon dioxide. Ultimately it was envisioned that such catalysts could be made part of a solar-driven photoredox cycle by coupling metalloporphyrins with semiconductor systems. Such a system would provide the energy required for CO₂ reduction to methanol, which is an uphill 6-electron reduction. Molecular modeling and design capabilities were used to engineer metalloporphyrin catalysts for converting CO₂ to CO and higher carbon reduction products like formaldehyde, formate, and methanol. Gas-diffusion electrochemical cells were developed to carry out these reactions. A tin-porphyrin/alumina photocatalyst system was partially developed to couple solar energy to this reduction process.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

ACKNOWLEDGMENTS

We would like to acknowledge the assistance of several colleagues who were instrumental in the success of this project. Dr. Craig Medforth and graduate students in the laboratory of Dr. Kevin Smith, in the Chemistry Department of the University of California at Davis worked very hard to synthesize the complex new catalysts developed in this work. They also provided analysis of these materials, particularly the NMR characterization. Dr. J. Martin E. Quirke, in the Chemistry Department of Florida International University, synthesized the complex hydrogen-bonding porphyrins. Professor Jose Colucci, of the Chemical Engineering Department of the University of Puerto Rico-Mayagüez, introduced us to the use of gas-diffusion electrodes in electrochemical cells.

TABLE OF CONTENTS

ABSTRACT	1
ACKNOWLEDGMENTS	1
TABLE OF CONTENTS	2
INTRODUCTION	2
BACKGROUND	3
EXPERIMENTAL	7
RESULTS	9

INTRODUCTION

Two major concerns currently in the United States are our energy future and protection of the environment from the harmful effects of greenhouse gases and global warming. As our natural fossil energy sources dwindle and concern about the pollutants produced by their combustion (namely CO₂) increases, it is time to seriously begin considering alternative energy sources and transportation fuels that are renewable and environmentally compatible. Such considerations have given new impetus to chemical storage of solar energy. In particular, chemical reactions that remove carbon dioxide from the atmosphere are attractive. Solar conversion of atmospheric carbon dioxide to clean fuels such as methanol can be achieved in a cycle that would add no net CO₂ to the atmosphere. In addition to the environmental advantages, conversion of CO₂ to methanol is economically attractive since methanol contains substantial energy, it is compatible with current transportation systems and it provides a source of feedstocks for production of useful organic chemicals. Methanol can also be used in a commercial methanol-to-gasoline (MTG) process. One approach to closing the fuel cycle is to utilize a renewable energy source to convert carbon dioxide produced from the combustion of fossil fuels back to fuel that can be used again. By doing so, we will not only generate a renewable fuel resource, but also close the CO₂ cycle and thereby reduce harmful greenhouse effects.

Carbon dioxide is a very stable molecule, and its direct reduction has a high activation barrier. Thus, catalysts to facilitate the conversion to 2-, 4-, 6- or even 8- electron reduction products are necessary in order to make this process viable. A number of organometallic compounds, including porphyrins and cyclams, have previously been shown to have activity for CO₂ reduction. In order to develop better such catalysts, we proposed to use Sandia's molecular

design expertise to engineer metalloporphyrin catalysts for CO₂-activation by optimizing their interactions with the CO₂ substrate. The focus of the research was to use molecular modeling to design catalysts and photocatalysts to convert CO₂ to reduced intermediates such as CO, bicarbonate and carbonate and subsequently to convert them to methanol, formaldehyde, and formate. Since conversion of carbon dioxide to methanol is an uphill 6-electron reaction, it requires a source of energy. Therefore, solar-driven photoredox cycles utilizing the newly designed and tested catalysts were also identified.

Once such a catalyst system and photoredox cycle is identified, a total system for large scale utilization must also be developed for the desired process. Sandia has had extensive experience in developing photocatalysts for wastewater treatment, and has deployed test systems at Sandia. Thus, we proposed to use Sandia's engineering-scale expertise in photocatalysis to develop and enhance an entire process for using CO₂, water, and solar energy to produce methanol, a valuable transportation fuel, and other chemical feedstocks.

BACKGROUND

Researchers around the world, particularly in Europe, have been investigating pathways by which CO₂ can be made into valuable fuels such as methanol, methane and higher hydrocarbons. Much emphasis has been placed on gas-phase catalysis, similar to Fischer-Tropsch chemistry for carbon monoxide reduction. This is a valuable approach. Another approach involves CO₂ activation in aqueous media. This process requires energy input into the system in the form of light. Nature has perfected this process in plants, which capture and activate CO₂ to produce energy-rich molecules (*e.g.*, glucose) and other more complex organic structures like proteins and genetic material. Man's attempt to mimic this process is called artificial photosynthesis.

Photoredox reactions involving metalloporphyrin photomediators have been investigated for some years for the purpose of splitting water for the production of H₂. The goal is to design a system in which a photoredox cycle is coupled to methanol synthesis. Recent patents have been awarded to Sandia for a porphyrin-based photocycle and its use in alkane-to-alcohol conversion and H₂ generation from water splitting. More recently, we have used these porphyrins to photosensitize photocatalytic detoxification reactions mediated by TiO₂, thereby extending the portion of the solar spectrum used by the reaction into the visible light region and increasing the efficiency of the solar detoxification process. A reductive cycle in which the porphyrin sensitizer is reduced to the porphyrin radical π -anion is attractive for this purpose because the porphyrin can directly inject an electron into the conduction band of the TiO₂ semiconductor. That is, in a reductive cycle, the porphyrin anion itself may provide the reducing equivalents required for CO₂ reduction on TiO₂. The tin and antimony porphyrins discovered by Shelnutz (Shelnutt, J. A., U. S. Patent No. 4,568,435, 1986 and Kalyanasundaram, K.; Shelnutz, J. A.; Grätzel, M., *Inorg. Chem.* 1988, 27, 2820-2825) provide the only known efficient class of photosensitizers that operate *via* an efficient *reductive* quenching mechanism.

Biomimetic CO₂ Conversion.

Mimicking biological methanogenesis or acetogenesis using solar energy or an electrochemical process, instead of H₂, to drive the uphill reaction would provide a renewable source of clean fuels and feedstocks. Since atmospheric or waste CO₂ is the source of carbon, no net greenhouse gases would result. Thus, solar-driven biomimetic methanogenesis could potentially provide an environmentally sound source of chemical energy.

The catalysts would be used in a solar-driven CO₂-conversion process like that illustrated in Figure 1. The photochemical reaction on the left is the photoredox chemistry that produces the reductant, in this case a long-lived tin(IV)-porphyrin radical anion. In the cycle, a tin(IV)- or antimony(V)-porphyrin absorbs a photon of visible light resulting in the formation of the triplet excited state of the porphyrin. The porphyrin photosensitizer in its excited state is reduced by a sacrificial electron donor such as triethanolamine (TEOA). The resulting long-lived π anion of the porphyrin has a redox potential low enough to reduce MV²⁺, which can subsequently reduce the CO dehydrogenase enzyme analog (CoP) leading to biomimetic CO₂ reduction. The reduced CO₂ product can be one of a number of species (e.g., carbon monoxide, methanol, formaldehyde) or a multi-carbon product (e.g., acetate). After reduction of CoP, the photosensitizer anion (SnP⁻) returns to the resting redox state (SnP). Of course, the sacrificial electron donor in this example must be replaced by a commercially viable process (water oxidation to O₂ occurs at the same potential), but the reaction described serves as a starting point for investigating the carbon-dioxide activating reaction. A similar photochemically driven reaction that mimics biological photosynthesis and electron transfer to biomimetically oxidize hydrocarbons (instead of CO₂ conversion) has been described and patented by Sandia. ("Method for Improving Product Yields in Anionic Metalloporphyrin-based Artificial Photosynthesis System" J. A. Shelnutt, U.S. Patent No. 4,568,435, Feb. 4, 1986, and "Process for Light-Driven Hydrocarbon Oxidation at Ambient Temperatures" J. A. Shelnutt, U.S. Patent No. 4,917,784, Apr. 17, 1990). Another patent on this process has also been applied for.

The first step in one route for the conversion of CO₂ to methanol is to convert CO₂ to carbonate. This can be accomplished biomimetically using a synthetic analog of the enzyme carbonic anhydrase, which converts CO₂ to carbonic acid and bicarbonate. Bicarbonate thermally (or in the presence of weak acid) decomposes to carbonate, CO₂, and water. In a second step, carbonate can be photocatalytically reduced to methanol using an illuminated photosensitized TiO₂ dispersion. Both of these reactions provide opportunities for enhancement by designing

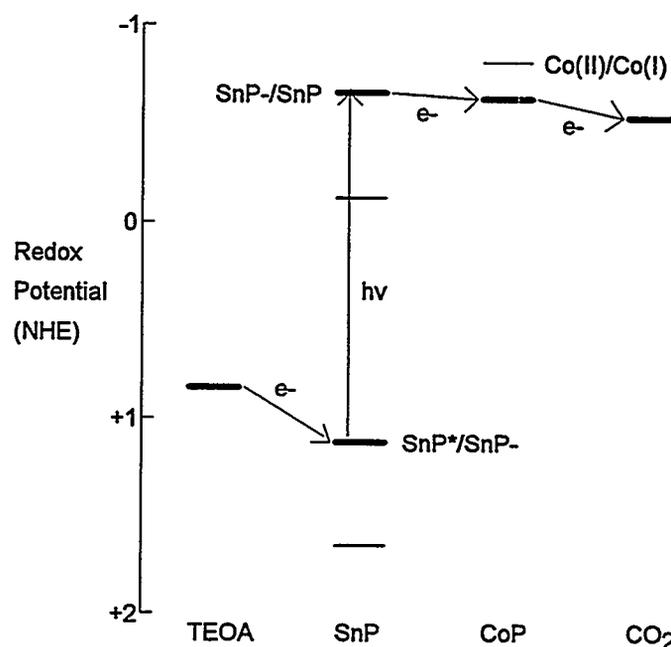


Figure 1. Energetics of a scheme for photochemical production of reductant to drive the reduction of CO₂. The SnP sensitized photoredox cycle is on the left; the Cobalt porphyrin CO₂-activation catalytic cycle is shown on the right.

catalysts and sensitizers that optimize reaction rates. For example, an engineered carbonic anhydrase analog containing a high affinity binding site for the CO_2 molecule could allow atmospheric CO_2 to be used as the source of CO_2 rather than concentrated sources. We already had considerable experience in using computer-aided molecular design (CAMD) methods to design CO_2 binding sites adjacent to catalytic metal centers. Zinc(II) porphyrin derivatives would provide carbonic anhydrase analogs, but designed CO_2 -binding porphyrins with other metals exhibiting CO_2 -activation chemistry provide other potential advanced catalysts for converting CO_2 to carbonate.

Although several photocathodes, including TiO_2 , have yielded photoreduction of CO_2 , the efficiencies have been relatively low. As is shown in Figure 2, the reduction potentials for the

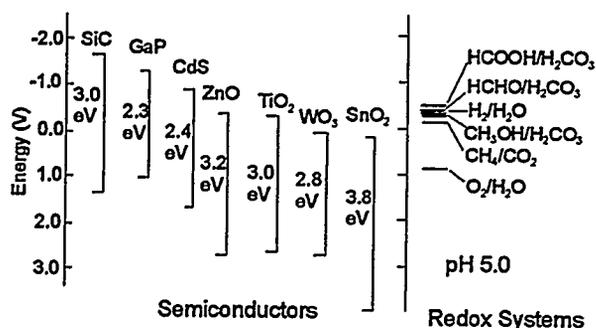


Figure 2 A schematic illustration of the energy correlation between semiconductor catalysts and redox couples in water. The bars for the semiconductors straddle their respective bandgaps. [T. Inoue, A. Fujishima, S. Konishi, K. Honda, *Nature*, 277 (1979) 637.]

multi-electron products of CO_2 sit very near the conduction band edge of TiO_2 . Reduction of CO_2 or an intermediate reduction product may or may not be possible, depending on many factors, such as the necessary overpotential to drive the reaction, and shifts of band edges relative to the carbon dioxide materials. However, Sandia has developed an extensive expertise in the photocatalytic detoxification of organic materials in water by coupling photosensitizers with semiconducting and non-semiconducting metal oxides. Use of photosensitizers which absorb visible light improves the solar efficiency of such processes, and moreover,

improvements in desired reaction rates have been observed.

For example, a wide variety of porphyrin and phthalocyanine photosensitizers are available for attachment to TiO_2 to enhance the portion of the solar spectrum used, providing an enhancement of approximately 20 fold in the use of solar energy. The metal can be varied to obtain the optimum redox potential for electron injection; substituents on the porphyrin ring can be varied to alter the interaction between the TiO_2 substrate and the photosensitizer as well as porphyrin chemical stability. The catalytic properties of the sensitizer may also play a role in the reaction, although this question has not yet been addressed in previous studies. Finally, it may also be advantageous to include a binding site for the carbonate substrate or intermediates in the carbonate reduction into the designed photosensitizer.

Sandia's initiation into TiO_2 photocatalysis began in 1989 when a method was proposed for solar photocatalytic detoxification of hazardous organic waste in water. Since then, an effective large-scale solar detoxification unit has been built and operated at Sandia and a rather large ongoing research and development program has arisen (\$6M in FY91 including Sandia and SERI). As part of this program, Sandia was investigating the potential application of solar photocatalysis to the simultaneous reduction of metal contaminants and oxidation of hazardous organics in contaminated water. As a result, we have gained significant expertise in the area of

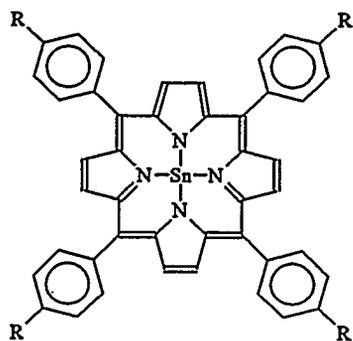
semiconductor photocatalysis, including metal-doped, dye-sensitized and bare TiO_2 . A well-equipped laboratory is set up and in operation.

We have also gained considerable experience with sensitization of TiO_2 through a related project funded through the University of New Mexico and the Waste Education and Research Consortium (WERC/DOE). Work carried out at Sandia for the WERC program has demonstrated 2-10 fold enhancement of photocatalytic detoxification using a porphyrin-sensitized

TiO_2 catalyst. A number of other useful properties of the porphyrin modified TiO_2 dispersions were discovered. The experience gained in the WERC program will be useful in efforts to design an efficient and stable photosensitized TiO_2 catalyst for CO_2 conversion. The porphyrins found to be most useful are the tin(IV) derivatives of the porphyrins shown in Figure 3.

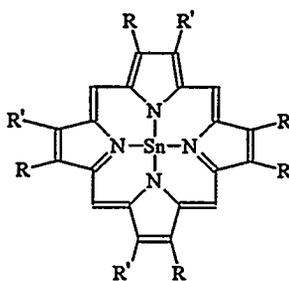
Another interesting finding resulting from the WERC study is the apparent "solubilization" of small TiO_2 particles by the adsorbed porphyrin. This effect favors higher photocatalytic activity in two ways. First, the surface area is increased by breaking up TiO_2 into small colloidal particles. Second, the

Sn(IV) Tetra(*p*-carboxyphenyl)porphyrin



R = COOH

Sn(IV) Uroporphyrin



R = CH_2COOH

R = $\text{CH}_2\text{CH}_2\text{COOH}$

Figure 3: Metalloporphyrin TiO_2 Photosensitizers.

adsorbed porphyrins provide a thin hydrophobic organic phase near the TiO_2 surface which may increase the affinity for various substrates (CO_2 , H_2CHO) in the reduction of CO_2 to methanol.

The porphyrins that were used in the WERC study have carboxylic acid substituents at the periphery of the macrocycle, which are known to interact strongly with the surface of TiO_2 ; thus, they may be adsorbed or attached covalently to photosensitize TiO_2 . Large enhancement in the rate of destruction of model toxin like salicylic acid has been found for the sensitized TiO_2 photocatalyst when using only visible light. We expect similar enhancements for the reduction of carbonate to methanol by using these porphyrin sensitizers.

As work on this LDRD progressed, it was recognized that the activation of carbon dioxide must be optimized prior to development of the full solar-driven system. This required a careful study of the electrochemical reduction of carbon dioxide by the newly developed catalysts. Figure 2 also provides relevant information about the reduction potentials of CO_2 in aqueous systems. In water, the relevant potentials are for the hydrated CO_2 , or carbonate species. [A complete chart of the equilibria for CO_2 and the standard reduction potentials is given in B.P. Sullivan, K. Krist, H.E. Guard, eds., "Electrochemical and Electrocatalytic Reactions of Carbon Dioxide", Elsevier, Amsterdam, 1993, p. 8]. A diagram showing the standard potentials for CO_2 reduction at pH 0 is given in Figure 4.

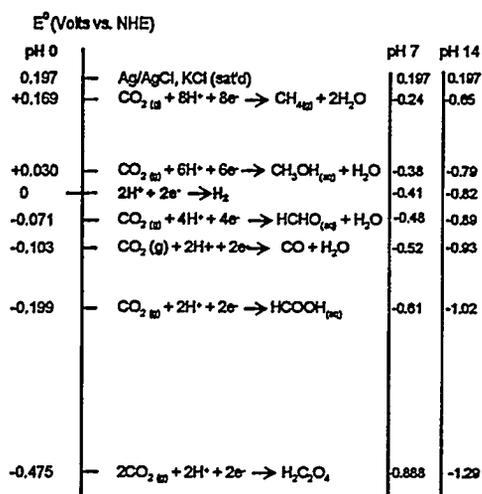


Figure 4 Carbon dioxide reduction potentials; Subtract 59 mV per pH unit for basic solutions.

As can be seen from this diagram, relative to hydrogen, the two- and four- electron reduction of CO_2 is only slightly uphill in energy terms. Moreover, relative to hydrogen, the production of methanol and methane are exoergic reactions. The direct one-electron reduction of CO_2 to the CO_2^- anion, however, requires the application of about 2 V, and thus represents a highly unfavorable pathway to the multi-electron products.

Since it is expected that electron-donating substituents will enhance the CO_2 reduction ability of the catalysts, we have an interest in those showing significantly more negative redox potentials.

Many cobalt and nickel macrocyclic compounds can catalyze the electroreduction of CO_2 . Our approach to developing new catalysts was to use the computer-aided molecular design (CAMD) methods being developed in the Fuel Science Department to optimize the properties of these catalysts. For commercially available cobalt porphyrins, the Co(II)/Co(I) couple, which may be the active catalytic redox species, is in the range from -0.8 (OEP) to -0.6 V (TPP). In addition to designing and constructing the required CO_2 binding cavity for our catalysts, we also have control over the redox potential by optimal choice of the porphyrin's substituents. To make the potential more negative, we add electron-donating substituents and to make the potential more positive we add electron-withdrawing substituents. We selected the dodeca-substituted porphyrins for the development of these CO_2 activation catalysts partly because we have more control over this redox potential, *i.e.*, a larger range of potentials can be attained for these porphyrins than is possible for more typical porphyrins. Since the exact redox potential requirements are not yet fully determined experimentally, we generated a series of catalysts using the dodeca-substituted porphyrins which have redox properties well outside the range of conventional porphyrin catalysts. The sum of the Hammett σ 's of the porphyrin substituents is being used as a measure of their electron withdrawing/donating abilities and, hence, the redox potentials. The range is from about -1.2 to about 1.64 for commercially available catalysts. By contrast, the dodeca-substituted porphyrins synthesized to date range from about -1.4 to 2.8. Synthesis is underway for porphyrins in an even larger range, and porphyrins in the range of -3.8 to 7.3 have been designed. New synthetic procedures for porphyrins have been a result of this LDRD project.

Other features of this new catalyst act to enhance catalytic activity. The new catalyst provides for (1) coordination of CO_2 at the cobalt(I) ion and (2) open axial coordination sites. Thus, these structural features meet the design goals of the CAMD efforts, which were based on recent detailed experimental studies of CO_2 reduction by the Ni and Co cyclam derivatives. We have successfully engineered all of these functionalities into the new catalysts designed over the last year.

EXPERIMENTAL

A modified ASTRIS Quickcell was used for the electrochemical experiments on CO₂. This cell is shown in Figure 5. The CO₂ electrode consisted of an Alupower [Electrosynthesis Corp.,

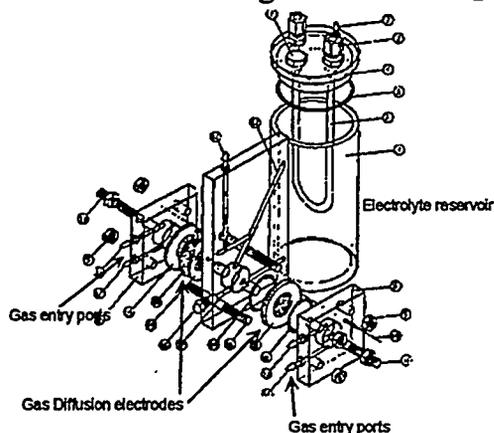


Figure 5 Schematic of ASTRIS Quickcell, taken from product literature. Astris, Inc., 2480 Dunwin Dr., Mississauga, Ontario, Canada L5L 1J9

Lancaster, NY] gas diffusion electrode modified with the Co-porphyrin catalyst. The Co-porphyrin catalyst was added by soaking the gas diffusion electrode in a pyridine or CS₂ solution of the catalyst. Product (CO) concentration was determined by gas chromatography. No CO product was observed from the cathode in the absence of the Co-porphyrin catalyst. CO conversions were calculated based on calibration of the gas chromatograph traces in which the volume of CO and of CO₂ was determined and were calculated as follows: [volume of CO/volume of (CO₂+CO)] *100. Initially, CO, H₂, and unreacted CO₂ were the products detected in the exiting CO₂ stream. No formaldehyde or methanol was detected by gas chromatography. In the modified cell which replaces the H₂ gas-diffusion anode with a platinum foil which oxidizes water, only a small amount of H₂ was detected in the CO₂ stream, indicating that there was substantial crossover of H₂ from the anode. However, H₂

is produced for electrodes with low coverages of Co-porphyrin catalyst.

Replacement of the H₂ electrode may also have contributed to the higher conversion efficiencies obtained with the new, modified cell. Current at the CO₂-reduction electrode was limited by the H₂ oxidation rate at the hydrogen electrode. This limitation was removed in the newer cell design. Up to 50% conversion to CO has been observed the current cell. Previously, no more than 5% of the CO₂ gas stream was converted to CO. A more controllable gas flow rate is also partly responsible for the higher conversion efficiency.

No significant difference is observed for electrodes prepared from pyridine and CS₂.

The cell was also been modified so that a smaller area electrode could be utilized. This meant that smaller amounts of the porphyrin catalyst could be tested. This was important since much smaller expenditures in resources is required and environmental, health, and safety concerns were reduced. In our standard catalyst test, 0.68 μmoles of catalyst were loaded onto the 5-cm² electrodes, providing roughly 0.14 μmole of catalyst/cm², or 8 μg of cobalt/cm².

Resonance Raman spectra were obtained using a partitioned Raman cell and a dual-channel spectrometer. The 413.1-nm line from a krypton ion laser (Coherent, INNOVA 20) and 457.9-nm and 528.7-nm lines from an argon ion laser (Coherent, INNOVA 20) were used for excitation in the Soret- and Q-band regions of the absorption spectrum. The scattered light was collected in the 90° scattering geometry. Polarized spectra were measured by passing the scattered light through a Polaroid sheet oriented parallel or perpendicularly to the polarization direction of the incident beam, followed by a scrambler in front of the spectrometer entrance slit. The spectral slit widths of the spectrometer were in the range of 2 to 6 cm⁻¹. The Raman cell was rotated at 50 Hz to prevent local heating of the sample and to probe alternately the sample and reference solutions.

Development of New Modeling Methods. We have been using Molecular Simulations' new CERIU² Version 1.6 and Bill Goddard's research version of POLYGRAF, which we obtained in working visits to CalTech, Pasadena, California. The latter program has quite a bit of functionality that was not in the commercial version. Some of these new capabilities are vital to our goal of developing a molecular mechanics force field for porphyrins that accurately predicts not only the conformation of the molecules but also the energies and vibrational spectra of the various conformer (local minima). We have completed the computer-optimization of the our molecular mechanics force field to the experimental data. We have also re-optimized the force field because of a minor error that has been in POLYGRAF from the beginning. This new force field corrects a minor problem in treatment of the metal in earlier versions and uses a periodic cosine function for the angle-term of the metal. This improved force field was used in the calculations reported in *J. Am. Chem. Soc.* manuscript. This new force field was converted to a format acceptable for the new CERIU² 1.6 program, and we used this program for our routine molecular modeling and design work.

RESULTS

Preliminary tests of TiO₂ and TiO₂/Fe-Phthalocyanine photocatalysts for CO₂ conversion were carried out in FY92. We also developed a photocatalytic system that utilizes both UV and visible light and that has redox properties capable of reducing CO₂. We were not able to reproduce literature report of CO₂ conversion using this system so other approaches were explored.

We have demonstrated that the integrity of the CO₂ cavity is maintained under solution conditions by obtaining H-NMR spectra of the paramagnetic cobalt(II) derivative for an analog of the catalysts in Figure 22 and Figure 23. To determine the catalyst structure in solution, we developed a new NMR method. The new method has been highly successful and may prove to be of general applicability. By this new method, the solution conformation is determined by comparing the experimental NMR spectrum with calculated NMR spectra based on the different possible conformers (local minima) calculated by the molecular mechanics calculations. Usually only one of the possible conformers gives a calculated spectrum that matches the experimentally obtained spectrum.

We have also experimentally determined binding energies of CO₂ relative to various solvent molecules by using ¹³C-NMR spectroscopy. The results of these paramagnetic relaxation measurements for two dodeca-substituted porphyrins, one possessing a binding cavity for small molecules like CO₂ (OETPPF₂₀) and another without the pocket (OMTPP) are summarized in Figure 7. NMR studies of substrate binding to these octaalkyl-tetraphenylporphyrin (OATPP) catalysts were undertaken. The binding energy of CO₂ is similar for both catalysts for similar sized solvent molecules like CO₂ and dichloromethane, although the binding differs for the two substrates; however, the binding energies of larger molecules like chloroform and benzene are reduced for the catalysts with the pocket relative to the one without the CO₂ cavity. The difference between the binding energies for all substrates and CO₂ are apparently low (< 1 kcal/mol) in solution, so we have now designed the improved catalysts described above.

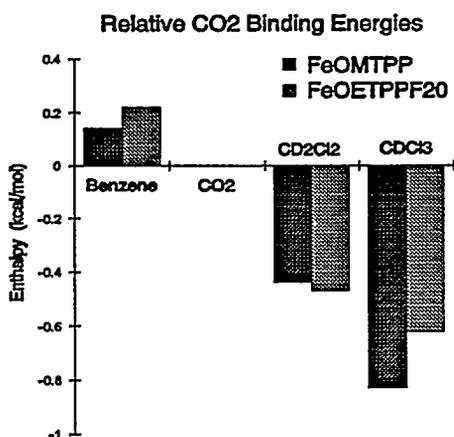


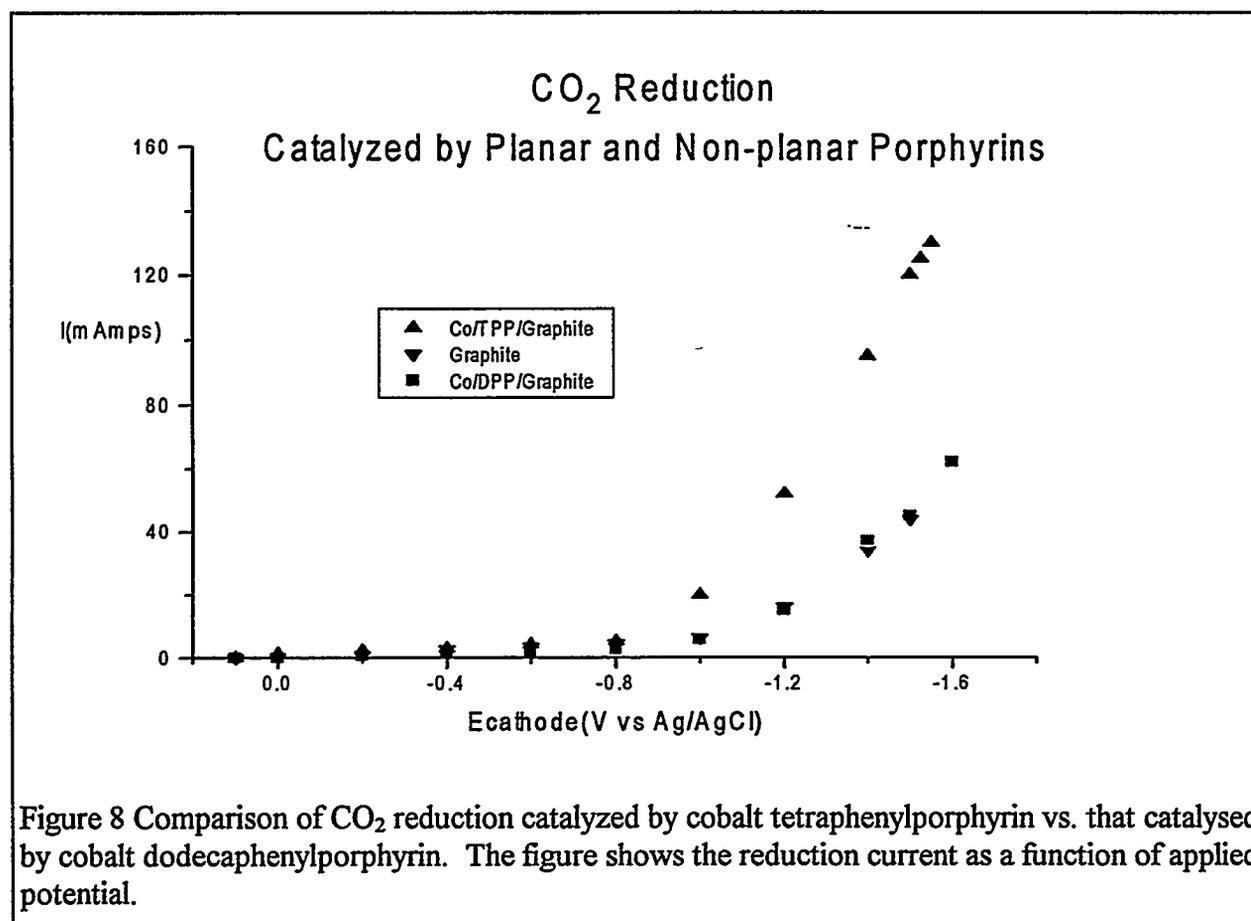
Figure 7. Enthalpies for binding various substrates relative to CO₂ obtained from ¹³C-NMR paramagnetic relaxation rates as a function of temperature.

The difference between the binding energies for all substrates and CO₂ are apparently low (< 1 kcal/mol) in solution, so we have now designed the improved catalysts described above. One possible further improvement that might be made to the catalyst in Figure 22 is to tighten the binding cavity. This will improve binding affinity for CO₂ while lowering the affinity for the larger substrates.

The photochemical reaction requires a photocatalyst, in addition to the CO₂-activation catalyst, which provides the reducing equivalents for CO₂ reduction. Because of the complexity of this combined catalyst-photocatalyst system using TiO₂ and tin-porphyrin/Al₂O₃ as photocatalysts, we proceeded to develop the photocatalyst system separately. The optimization of a potential photocatalyst for the reduction of CO₂ has been completed (FY93 objective 2) and is described in a *Solar Engineering*¹ paper that has been published. A patent application is currently being prepared for this tin-porphyrin/alumina photocatalyst system for this and other applications. The energy for the reaction can come either from a light-driven (solar photochemical) reaction or from an electrode (electrochemical) reaction. Consequently, we immediately undertook the development of an electroreduction apparatus so that more controlled activity tests could be carried out.

RESULTS OF ELECTROCHEMICAL REDUCTION OF CO₂

Data from the electrochemical reduction of CO₂ using the simplest planar and non-planar porphyrins are shown in Figure 8. An increased cathodic current for a given applied voltage is obtained for the electrode treated with the cobalt tetraphenylporphyrin (CoTPP) relative to the blank, untreated electrode. When using the CoTPP, the current “turns on” at about -1.0 V vs. Ag/AgCl, while for the blank, this turn-on point is about -1.2 V vs. Ag/AgCl. The electrode treated with cobalt dodecaphenyl porphyrin shows the same performance as the blank, suggesting that no catalytic activity is obtained for this non-planar porphyrin.



Furuya², among others, has measured the reduction of carbon dioxide using metal phthalocyanines and copper metal loaded gas-diffusion electrodes. Thus, it was of interest to also evaluate some of the readily available phthalocyanine catalysts. Data for the CoTPP and Copper and Cobalt phthalocyanines is shown in Figure 9a. The CoTPP shows substantially larger reduction currents in the 0.5 NaHCO₃ electrolyte.

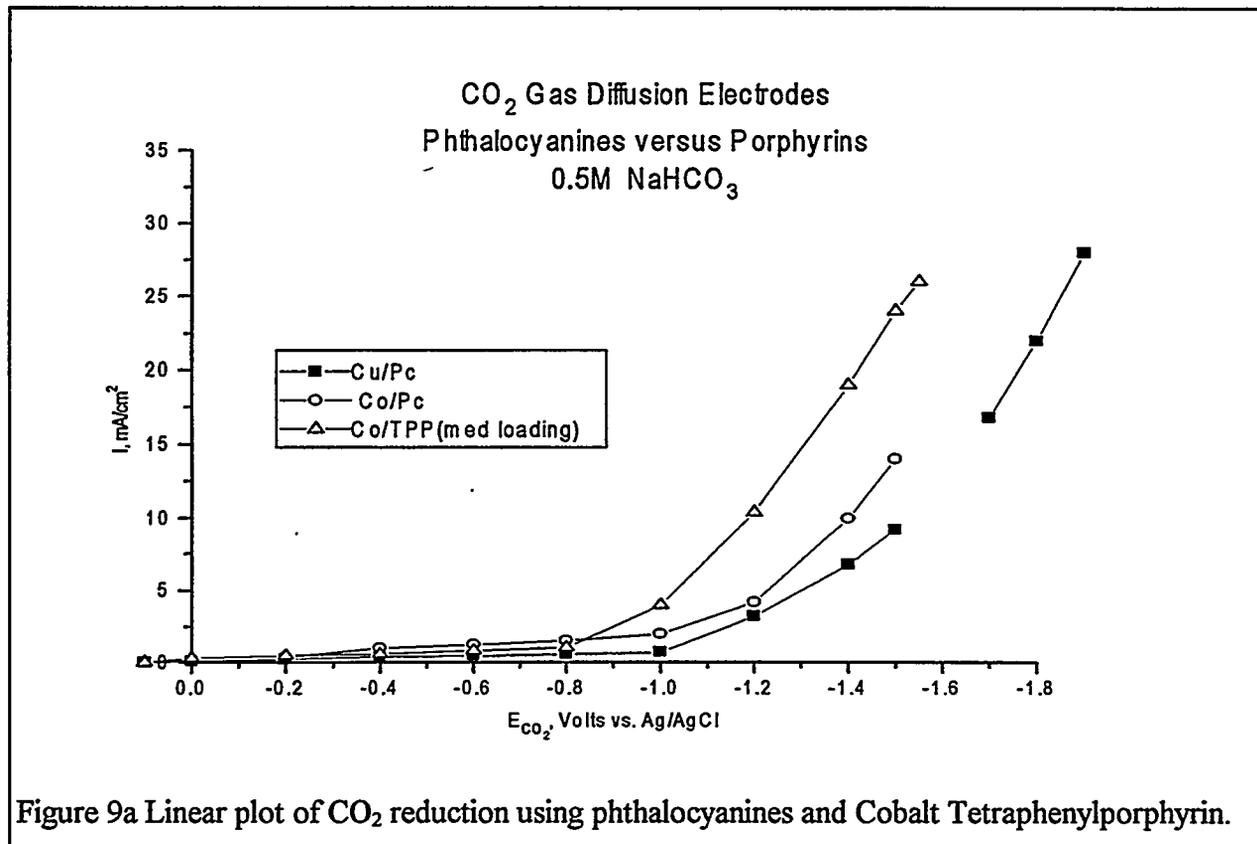


Figure 9a Linear plot of CO₂ reduction using phthalocyanines and Cobalt Tetraphenylporphyrin.

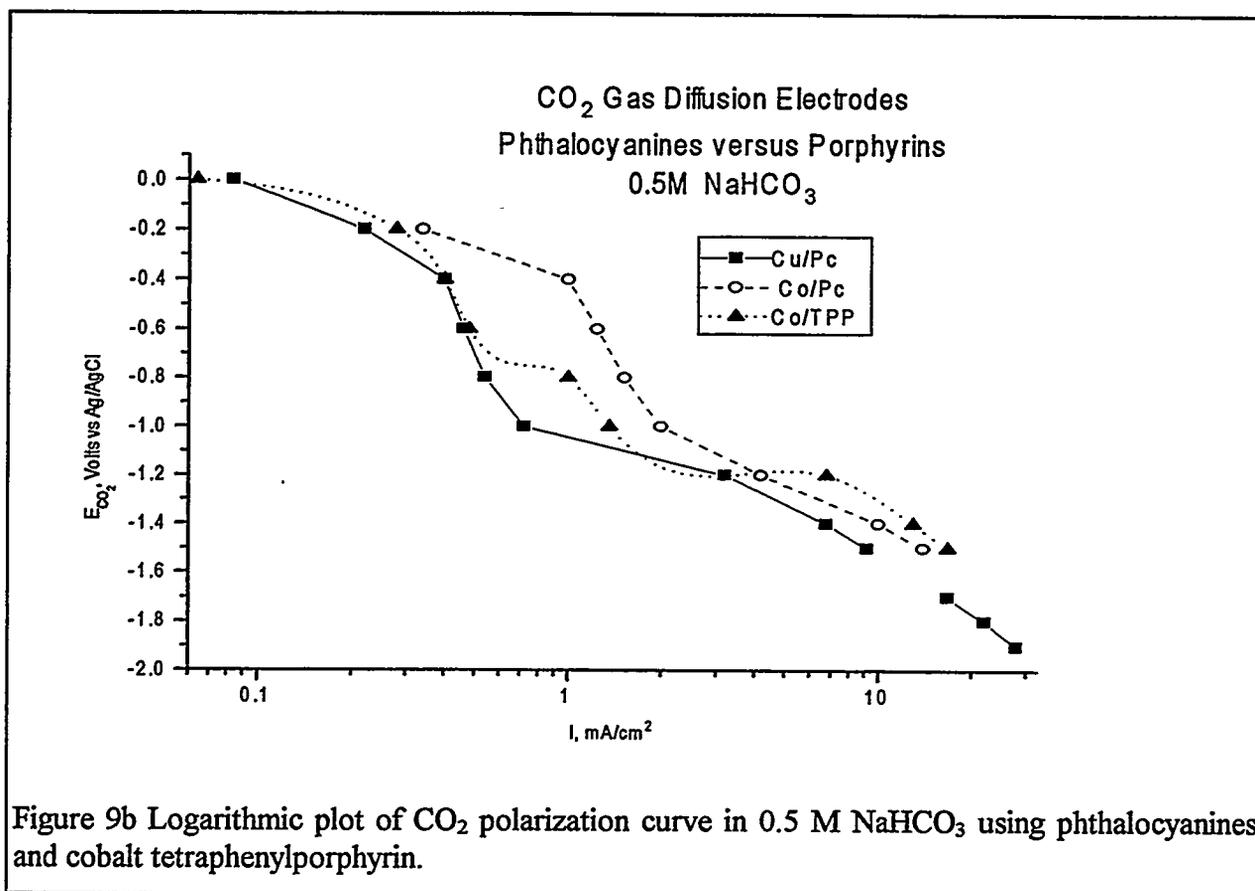
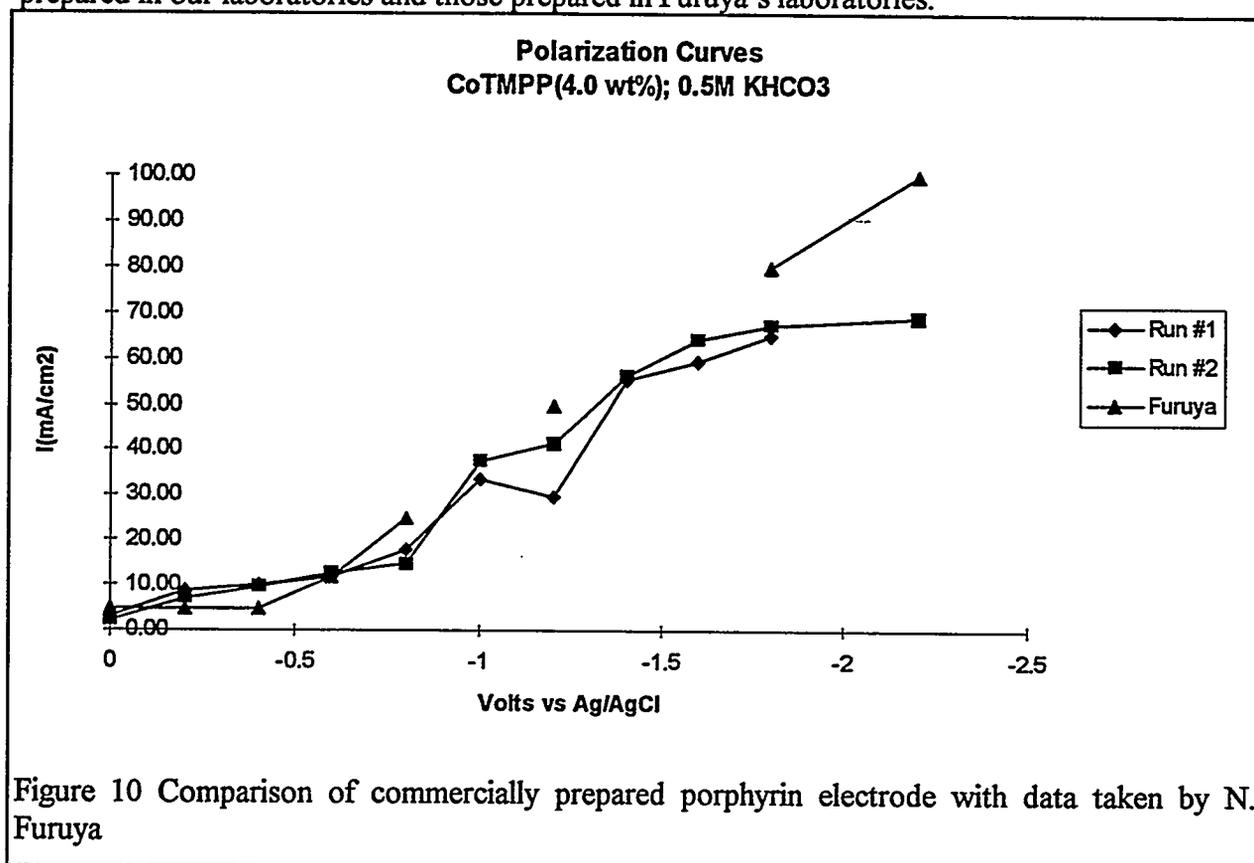
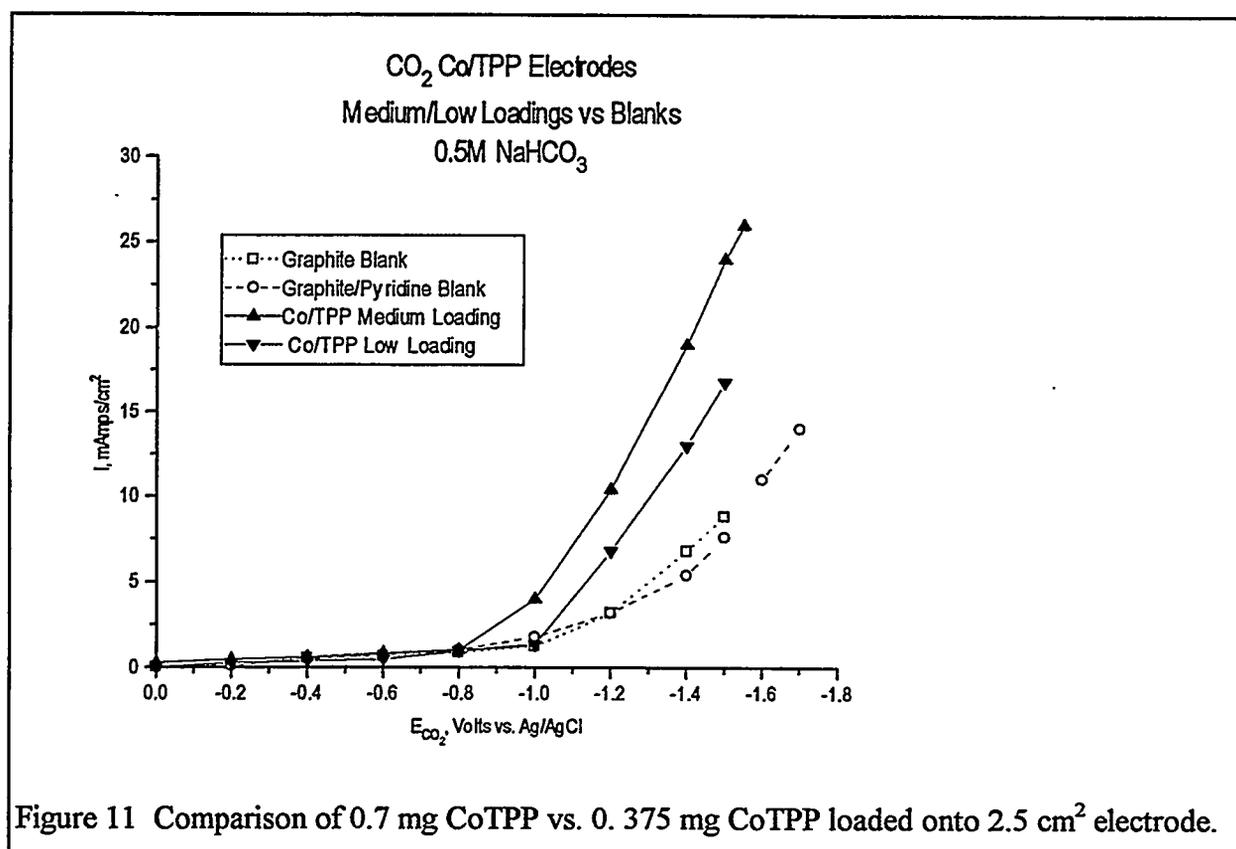


Figure 9b Logarithmic plot of CO₂ polarization curve in 0.5 M NaHCO₃ using phthalocyanines and cobalt tetraphenylporphyrin.

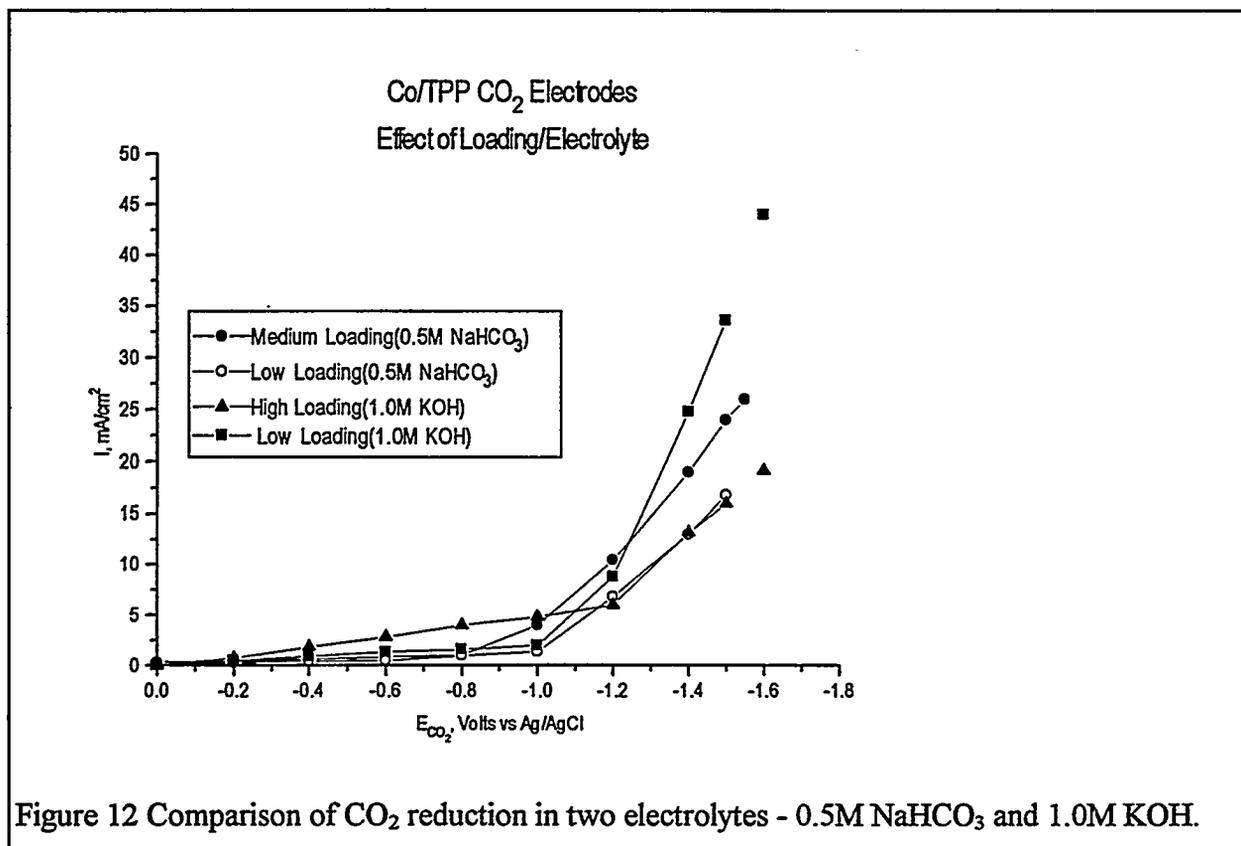
Cobalt porphyrins, as well as iron porphyrins, have also been used for oxygen reduction in fuel cells, and as a result, one commercially prepared porphyrin-loaded gas-diffusion electrode is available from Electrosynthesis Corporation.³ The porphyrin used by Electrosynthesis Corporation is the planar cobalt tetramethoxyphenylporphyrin (CoTMPP). In order to determine whether commercial preparation significantly increased catalytic activity, a sample of the commercially prepared CoTMPP electrode was run in our cell. These data are plotted in Figure 10 along with data taken from Furuya's paper cited above for comparison. It can be seen that current densities of approximately the same order or magnitude are achieved for electrodes prepared in our laboratories and those prepared in Furuya's laboratories.



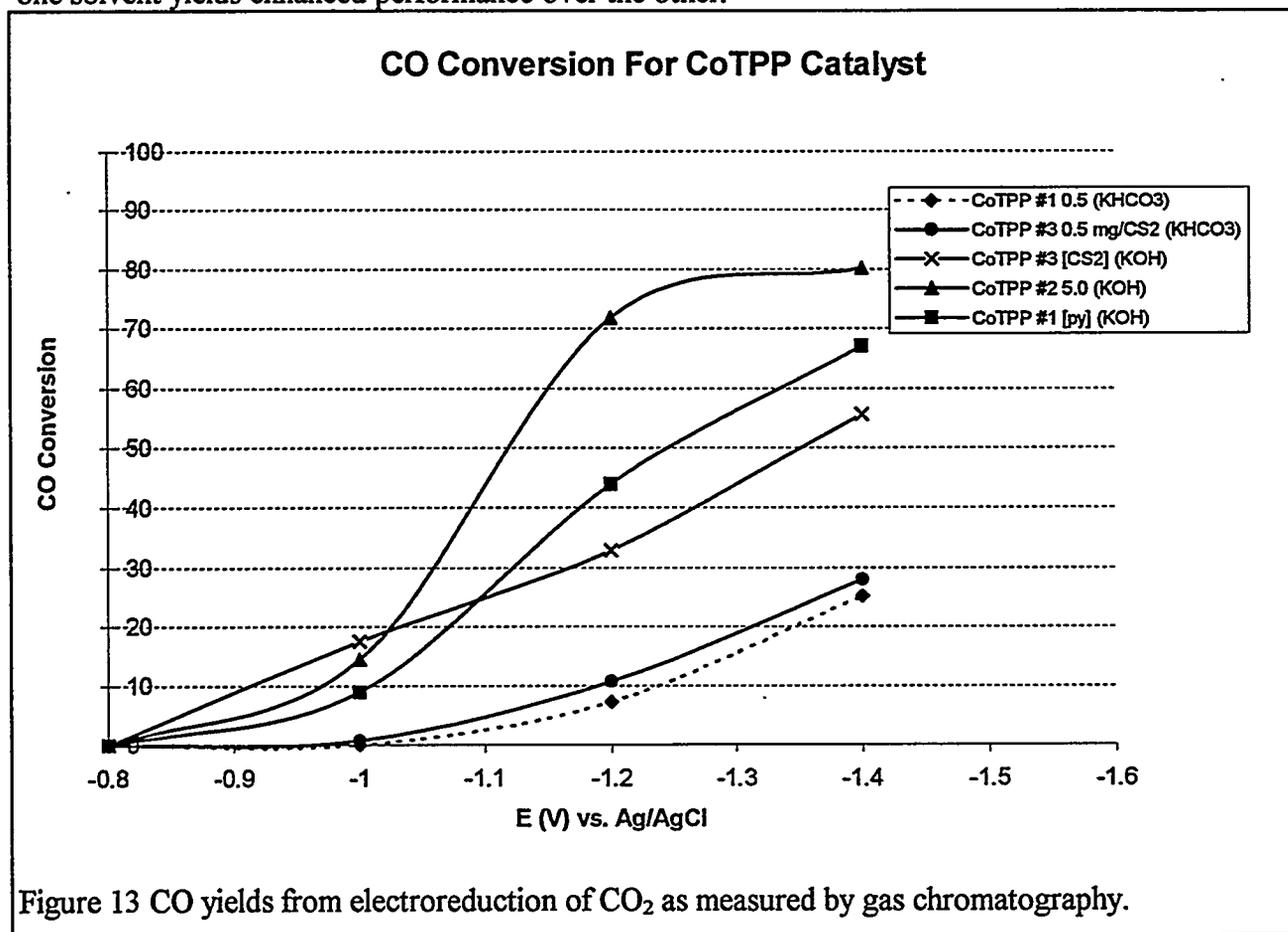
As noted above, in our standard catalyst test, 0.68 μmoles of catalyst are loaded onto the 5- cm^2 electrodes, providing roughly 0.14 μmole of catalyst/ cm^2 , or 8 μg of cobalt/ cm^2 . This loading is referred to as our "medium" loading. When ten times this amount of catalyst is loaded on the surface, no more than double the activity is observed, which indicates we are using the lower loading of catalyst effectively and that additional loading is wasted. For comparison, in other gas-diffusion electrode applications using platinum, the lowest catalyst metal loadings used are 20 $\mu\text{g}/\text{cm}^2$. Several runs were done at "low" (0.375 mg), "medium" (0.7 mg) and "high" (50 mg) loadings of the catalyst. In the "high" case, the porphyrin or phthalocyanine material could be clearly seen as a dried powder on the surface of the gas diffusion electrode, and it is believed that much of this material is wasted. Figure 11 shows that the medium loading of catalyst resulted in more reduction than did the low loading, and both were better than the blank, or the pyridine-treated blank electrodes.



In addition to the loading, we examined whether a change in the electrolyte influenced the CO_2 reduction efficiency. As shown in Figure 12, the results in bicarbonate solution (marked by circles in the Figure) are not significantly different from the results in KOH solution.



Having measured reduction currents as a function of applied voltages, we utilized a gas chromatograph to determine what the products of this electroreduction current were. Figure 13 shows CO conversion yields as a function of applied voltage. These data were taken using catalyst loadings of 0.5 mg and 5.0 mg per electrode. The data compare results for different catalyst loadings, different electrolytes and different electrode preparations. Data denoted by [CS₂] were prepared using carbon disulfide as the catalyst solvent. It was thought that perhaps the pyridine solvent was binding to the porphyrin and blocking a potential CO₂ binding site. However, no significant changes in CO₂ reduction were noted as a function of catalyst loading solvent, as can be seen by comparing the first two curves listed in the legend in Figure 13. Performance in KOH versus that in KHCO₃, however, appears to be better for CO production. Of the three shown as the last three curves listed in the legend in Figure 13, the best performance was observed for the electrode denoted CoTPP #2 5.0 (KOH) in Figure 13, for which 5 mg of CoTPP were loaded onto the electrode, in a "high" loading. The third and fifth curves listed in the legend differ only in the catalyst solvent, and while different, do not unequivocally show that one solvent yields enhanced performance over the other.



Advanced Porphyrin Systems

Synthesis of the iron and cobalt derivatives of the fluorinated dodecaphenylporphyrins (DPP) was successful and yielded quantities suitable for catalyst testing. This required the scaled-up re-synthesis of the entire series. The compounds are: CoDPP, CoDPPF₈, CoDPPF₂₀, and CoDPPF₂₈. These halogenated porphyrins are of interest because of their (1) high stability, (2) the presence of a CO₂-binding cavity, and (3) their novel electronic properties, which will extend the range of redox potentials for this series in the negative direction. Figure 14 shows the iron analogs of the dodecaphenyl systems that were also evaluated in this study.

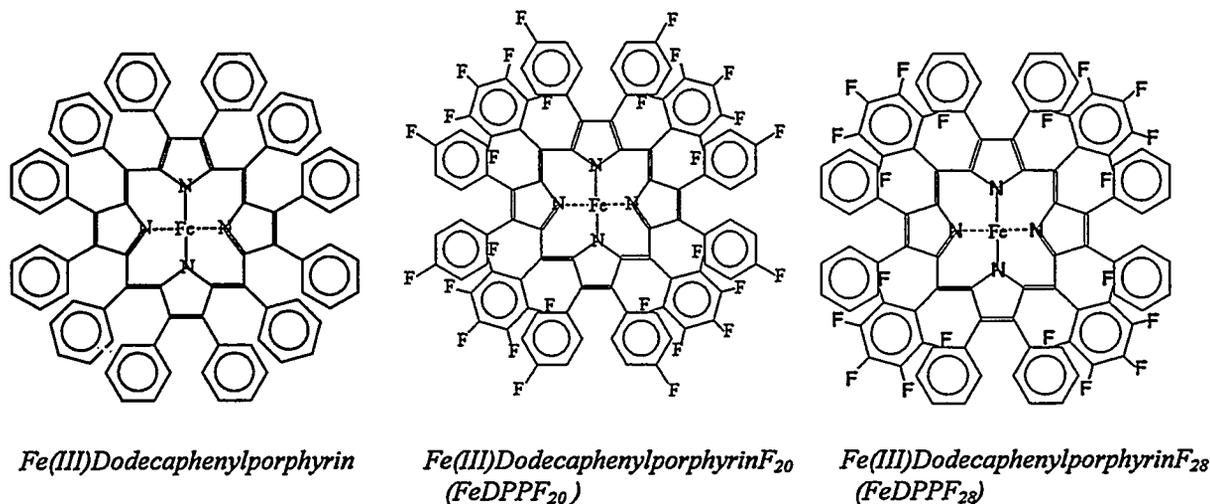


Figure 14 Dodecaphenyl porphyrins

Efforts are still underway to synthesize more highly fluorinated versions of CoDPP via the Suzuki reaction (see Figure 15).

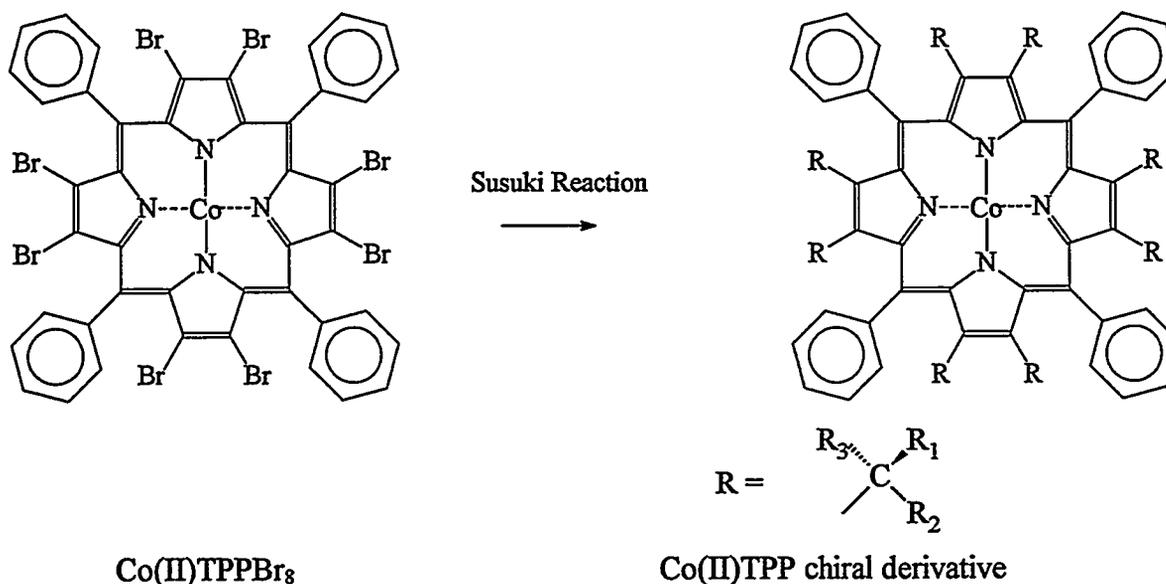
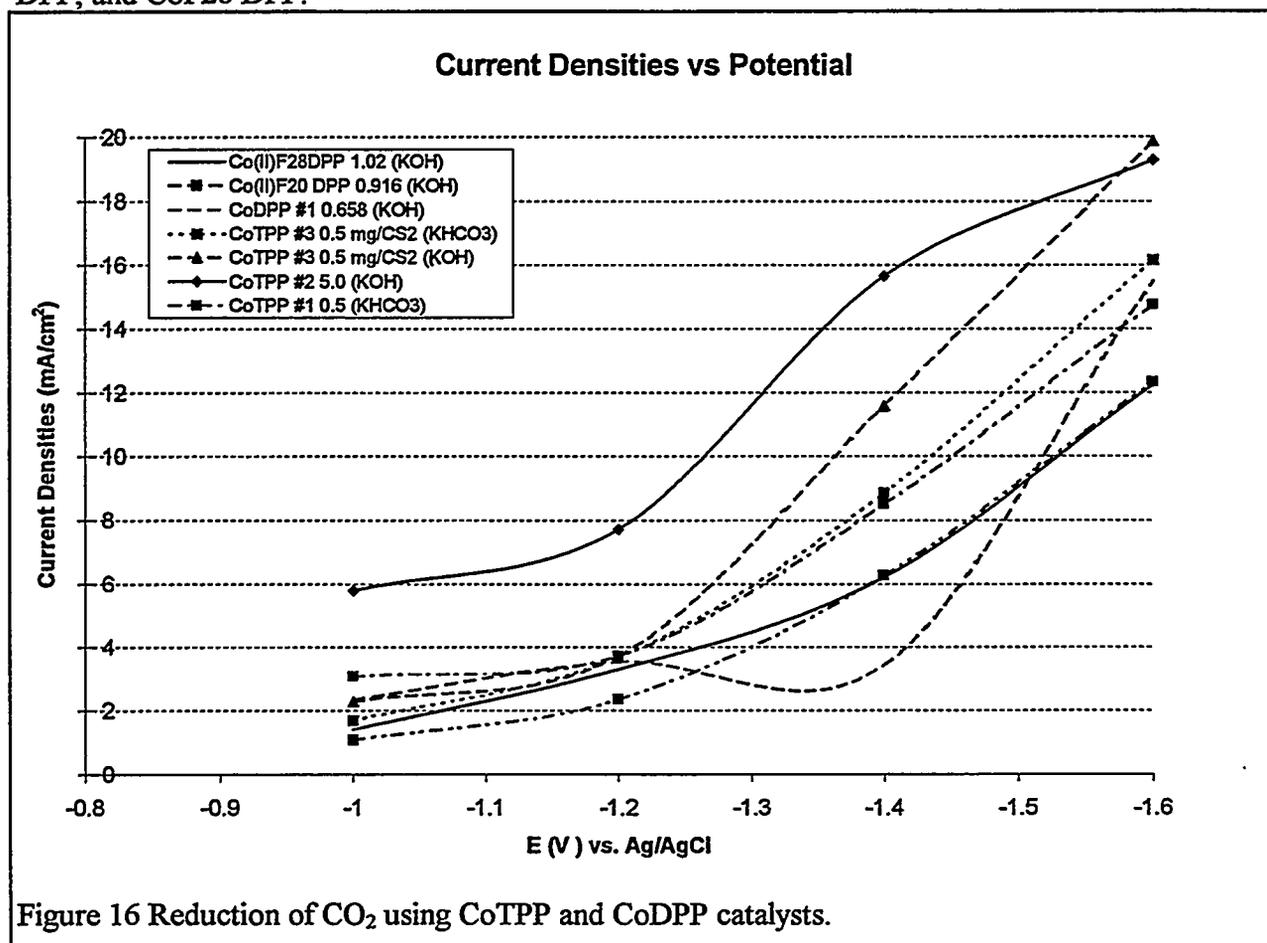
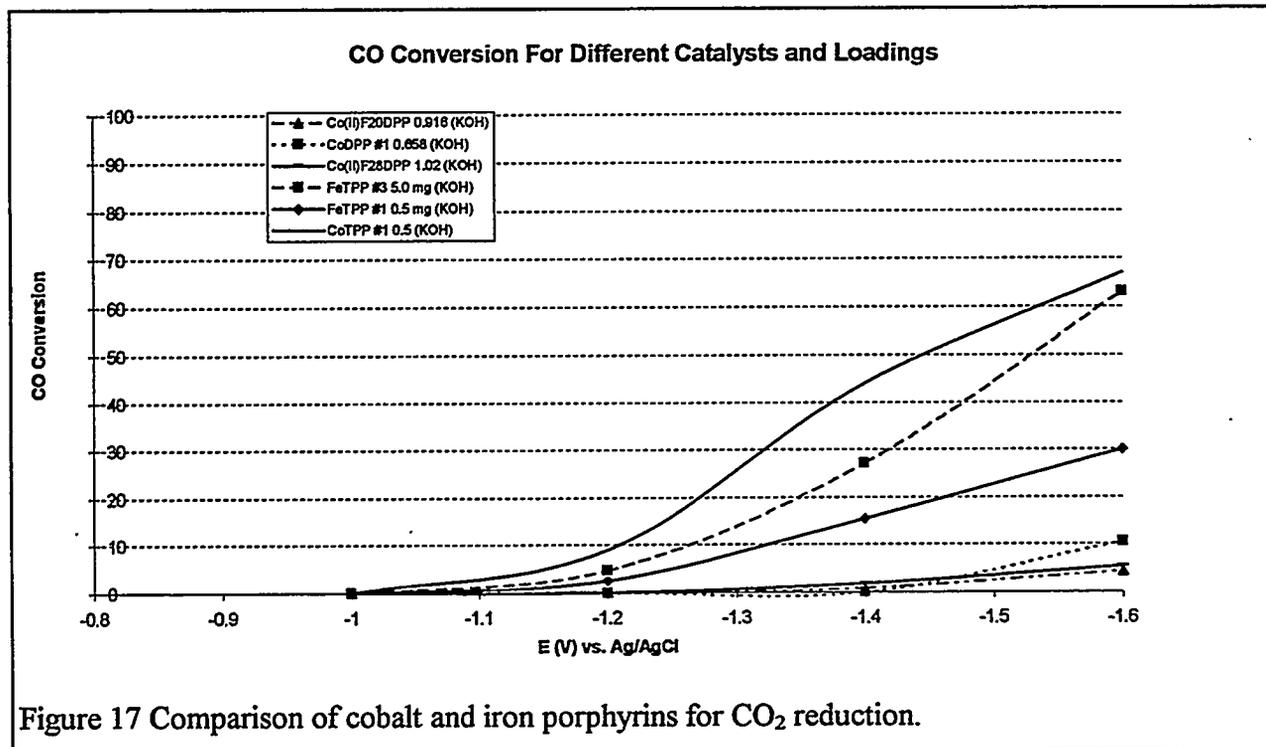


Figure 15 The synthesis of cobalt derivatives of tetraphenylporphyrins with chiral pyrrole substituents.

Figure 16 compares current densities for the reduction of CO_2 by electrodes catalyzed by the CoTPP and the non-planar cobalt dodecaphenylporphyrin, and its fluorinated analogs, CoF20 DPP, and CoF28 DPP.



Porphyrins and phthalocyanines containing most metal centers have been studied for the activation of small molecules such as O_2 and CO_2 . Of these, iron and cobalt are frequently found to be the most active. Figure 17 compares the results obtained for the FeTPP and compares it with the CoDPPs and the CoTPP. Again, it was observed that CoTPP resulted in the greatest amount of CO produced.



Using the CO yields as determined from the gas chromatography it was possible to compare CO current efficiencies for different catalyst systems. Figure 18 shows measured current vs. voltage for seven different electrodes. The percentage labels on the chart are the CO current efficiencies measured while holding the applied potential on the working electrode at -1.6 V vs. Ag/AgCl. No CO was measured for the CoDPP in KOH, the blanks run in KHCO₃ and KOH, and the FeF20TPPCI catalyst run in KHCO₃. The highest conversion efficiencies were obtained for the CoTPP in KOH and the CoOEP, also in KOH, both of which are planar cobalt porphyrins. Finally, the commercially prepared, planar CoTMPP also yielded moderately high conversions to CO, which we measured at 37% at -1.6 V vs. Ag/AgCl. The CoTMPP also had the highest current densities in this run, which means that other products were being produced, which we did not detect. It is possible that another main product was hydrogen, from the reduction of the water.

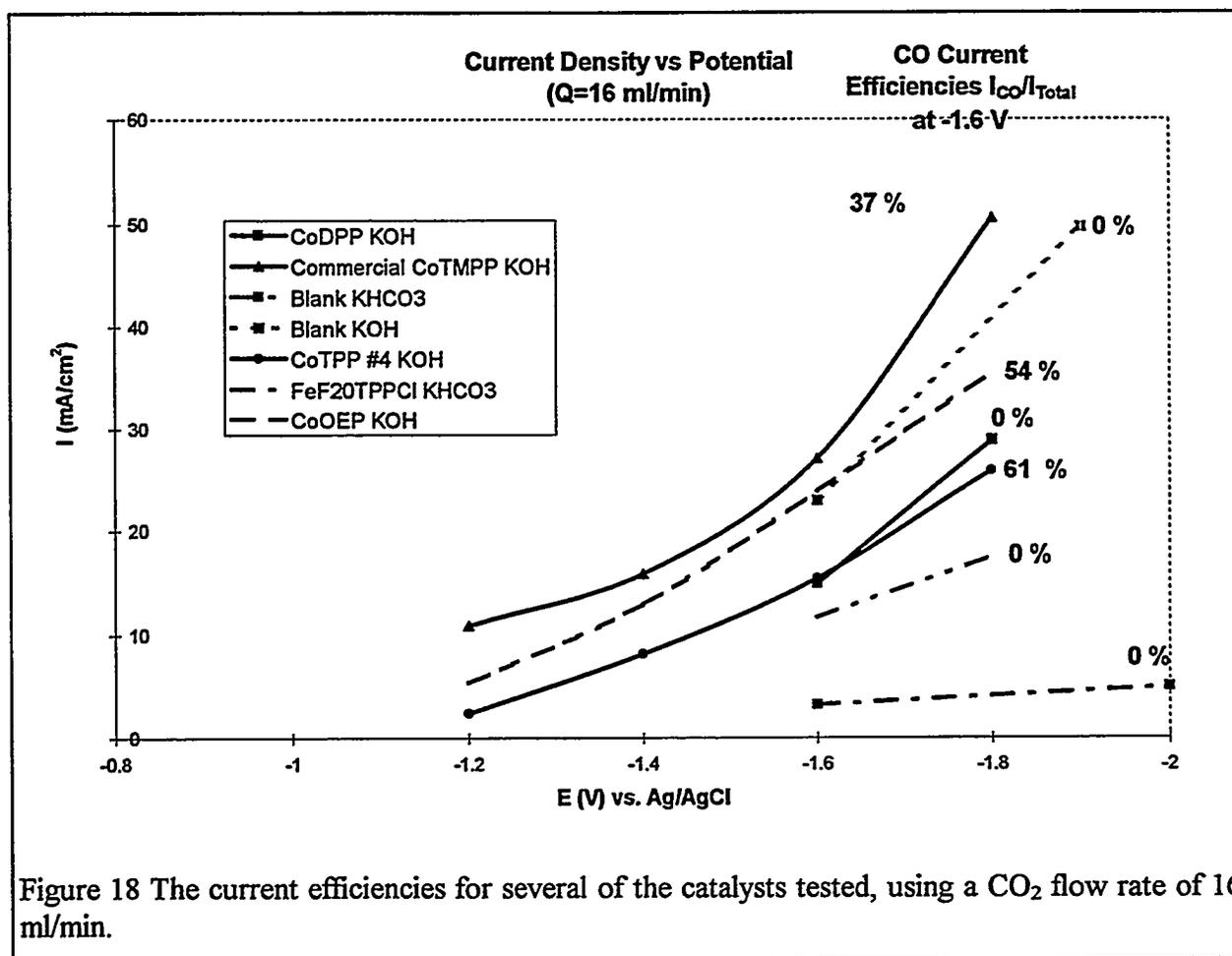
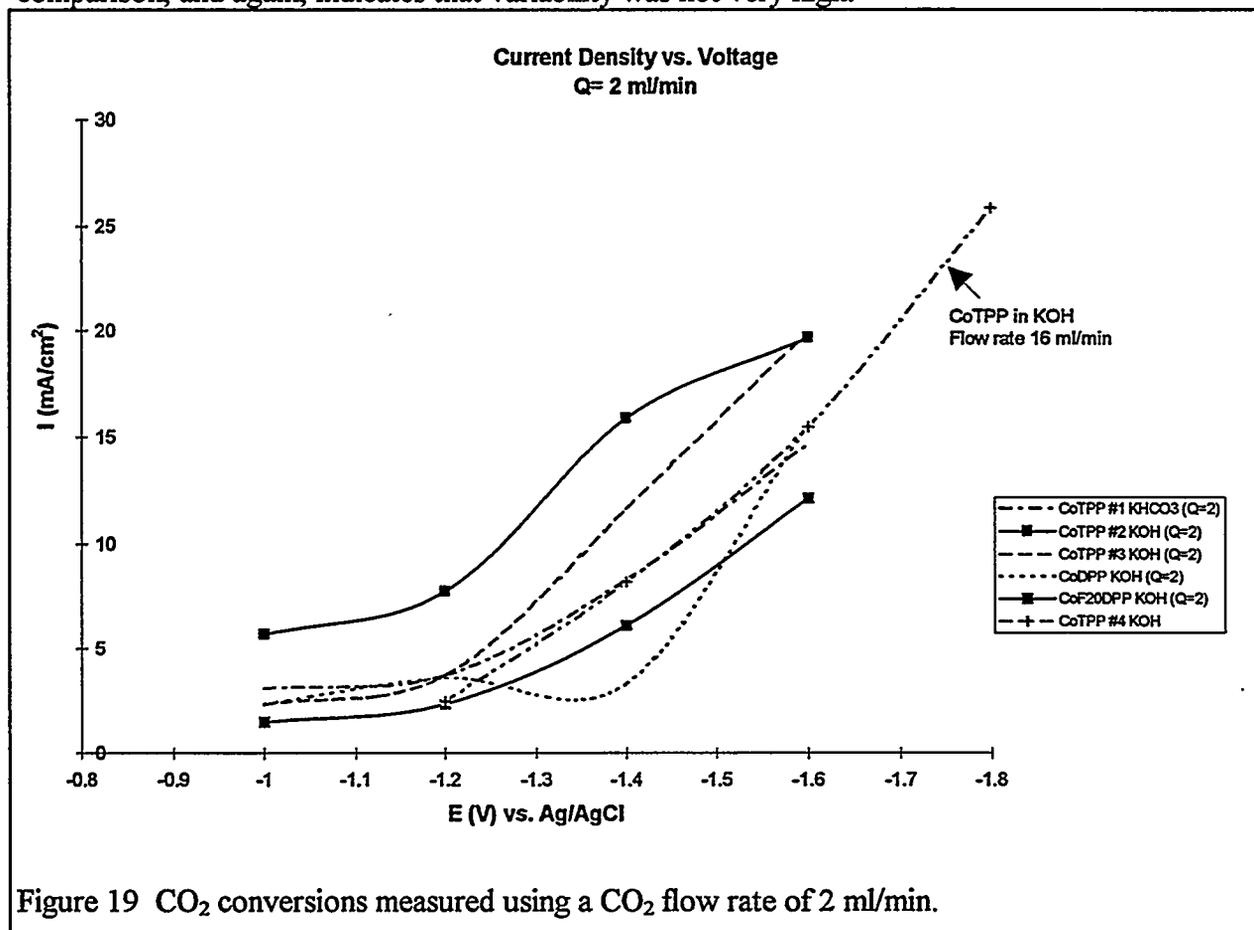
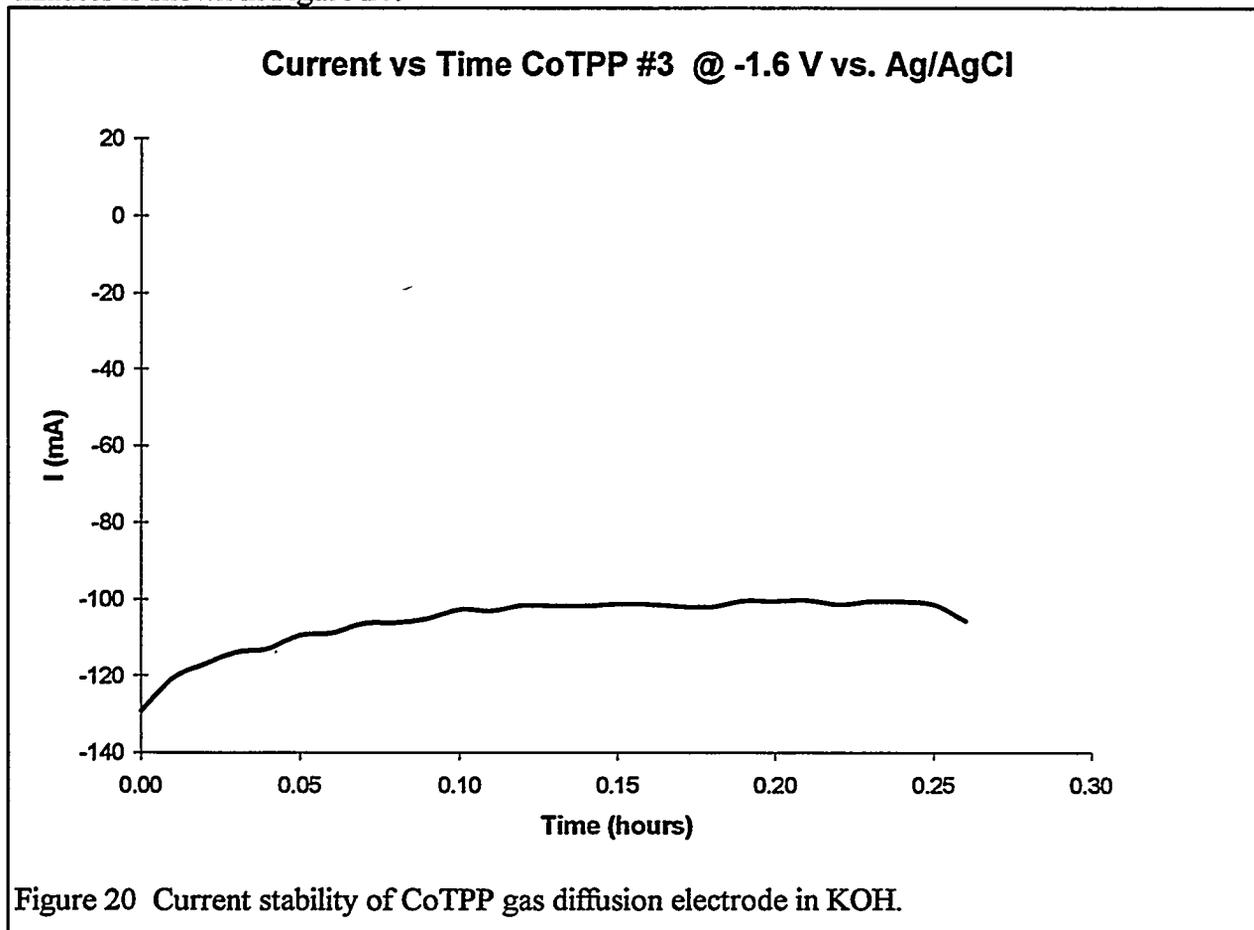


Figure 18 The current efficiencies for several of the catalysts tested, using a CO₂ flow rate of 16 ml/min.

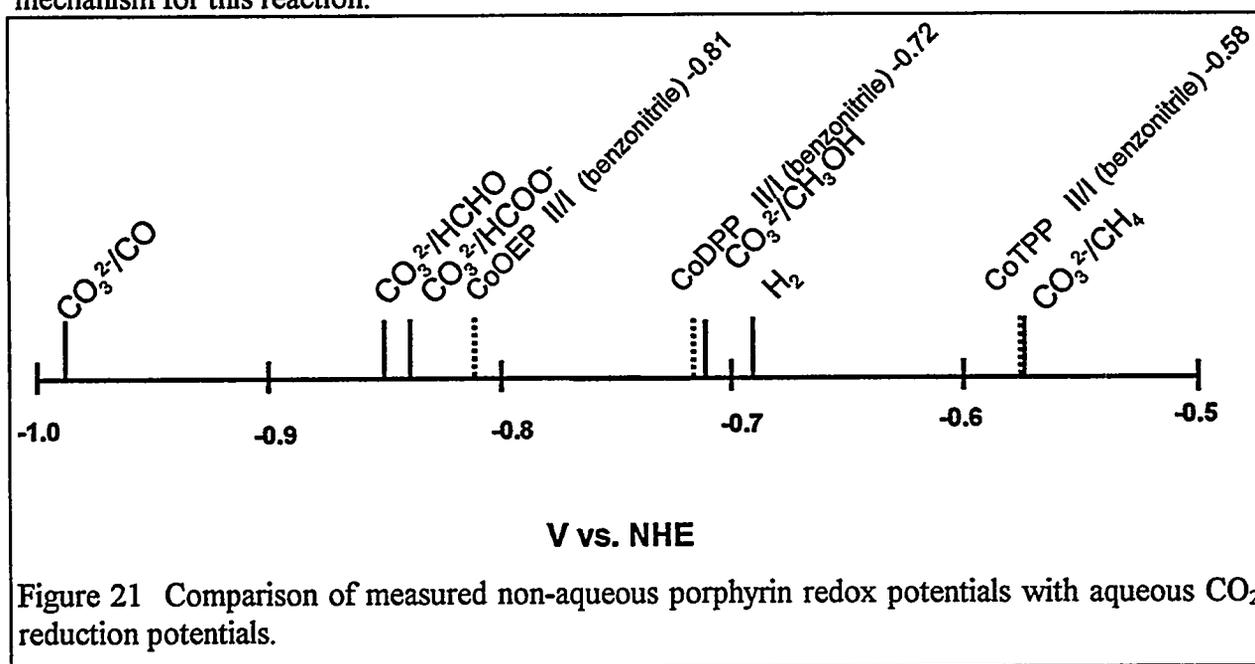
During the experiments it was observed that the CO_2 flow rate had an effect on the measured conversion efficiencies. Data using a flow rate of 2 ml/min, as measured by our in-line rotameter, is shown in Figure 19. The variation for the three different runs that are shown in this figure suggest that flow control was not very accurate. A flow rate of 16 ml/min is shown for comparison, and again, indicates that variability was not very high.



Finally, the stability of the electrodes was determined. A typical current trace over 15 minutes is shown in Figure 20.



In an effort to determine the effects of the redox potential on the catalytic activity, the redox potentials for the cobalt porphyrins were measured in a number of solvents. The values measured in benzonitrile for what are believed to be the II/I couple are shown in Figure 21, along with values for the relevant carbon dioxide species, corrected for a pH 12 solution. Since these potentials were measured in different solvents, it is misleading to make a direct comparison between them. However, it can be seen that the potential measured for cobalt dodecaphenylporphyrin is between the values measured for the two planar porphyrins, CoOEP and CoTPP. Moreover, they are all significantly more positive than the potential required for the reduction of the carbonate species present in a 1 M KOH solution to the CO, which is observed in our experiments. Thus, this does not provide direct evidence for a stepwise reduction of the cobalt species to the Co^I state, followed by transfer of the electron to the CO₂ species. Reduction of a porphyrin-CO₂ complex may be involved, but there is no direct evidence in these data of any mechanism for this reaction.



In addition to the non-planar dodecaphenyl porphyrins, several porphyrin catalysts with carboxylic acid groups like the one shown in Figure 22 were synthesized and characterized by NMR, UV-visible, and resonance Raman spectroscopy. Because of the crowding of substituents at the periphery, these porphyrins are also distorted into a saddle conformation which provides a small, rigid binding cavity at the metal site suitable for binding CO₂, CO₃⁻² or HCO₃⁻. (Furthermore, the tin derivatives of these porphyrins give photocatalysts which can be bound to supports like alumina through the carboxylate groups and which may provide enhanced photoreduction of CO₂.) Figure 23 shows the calculated structure of CO₂ bound to the ethyl-analog of the porphyrin in Figure 22. The new catalyst represents an improvement over earlier designs because it incorporates required hydrogen-bonding and other functionalities.

Calculations show that the hydrogen-bonding functionalities at each end of the cavity adds 1-3 kcal·mol⁻¹ of binding energy to the already significant binding energy coming from van der Waals interaction between CO₂ and the atoms lining the cavity of our previous designed catalysts. Also, we expect higher catalytic activity because the interaction with the NH groups at one end of

the cavity acts to stabilize an intermediate in the reduction reaction (Figure 23). The predicted structure of the CO₂ binding cavity has been verified for another analog of the catalyst (CoOETPP) by X-ray crystallography, and the X-ray structure also shows that a molecule (dichloromethane) is bound to this cavity.

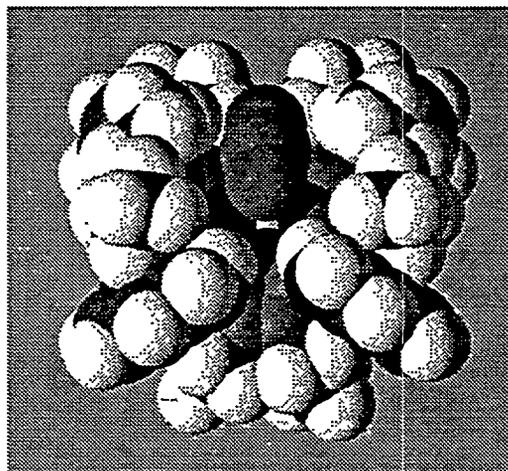
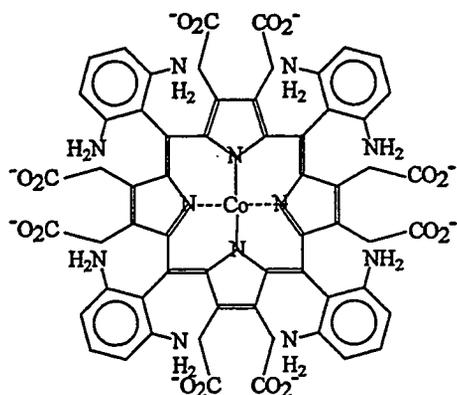


Figure 22. Newly designed CO₂- Figure 23. Energy-minimized complex between CO₂ and an activation catalyst with the structural analog of the catalyst in Figure 22. CO₂ is bound in a cavity features and properties desired for at the Ni atom (light blue). The upper oxygen (red) atom of electroreduction of CO₂ to CO, formate, CO₂ is hydrogen bonded to two NH groups behind the and more highly reduced products like oxygen atom. N(dark blue), H(white), C(gray). methanol.

The new catalyst was also designed to have favorable redox properties (< -0.8 V) for CO₂ reduction by providing a high enough overpotential to drive the reduction of CO₂ to CO. The first stage in the conversion of CO₂ to methanol is the reduction of CO₂ to CO. The reaction is $\text{CO}_2 + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{CO} + \text{H}_2\text{O}$ and has the redox potential of -0.52 V versus NHE at pH 7, based simply on the reactants and products involved. This is the limiting potential at which the two electrons must be delivered to CO₂ by the catalyst. However, in the absence of a catalyst, it is found that the actual electrode potential required is more negative than -2.0 V, thus, a catalyst is clearly needed. (Direct conversion of CO₂ to methanol occurs at only -0.38 V, but involves 6 electrons.) Even in the presence of a catalyst, the reductant that must be provided by the photocatalyst system or, for electroreduction, by the electrode must be more negative than -0.52 V.

Detection of Substrate-Catalyst Hydrogen-Bonding Interactions. Having observed no notable increase in CO₂ reduction using the non-planar porphyrins, we began to explore new porphyrins with hydrogen bonding groups, such as the porphyrin shown in Figure 24. Spectroscopic data has demonstrated hydrogen-bonding between substrate molecules and H-bond donor groups attached to the catalyst. H-bonding between substrate molecules and the -NH₂ group of 5-amino-octaethylporphyrin (5-NH₂-OEP) has been demonstrated by resonance Raman spectroscopy. The molecular structure of 5-NH₂-OEP is shown in Figure 24 and its resonance Raman spectra in the C-N stretching region of the amino group for various solvent conditions are shown in Figure 25. (Figure 25 also shows the spectrum of NiOEP (unsubstituted) for comparison.) H-bond formation is detected in the resonance Raman spectrum by the upshift in the frequencies and changes in relative intensities of several Raman lines in the region of the C-N

stretching vibration of the amino group. No other significant differences are observed in the spectra, indicating negligible effect of H-bonding on the porphyrin macrocycle. Of particular interest is the upshifts in the lines at 1260 and 1382 cm^{-1} and the decrease in the intensity of the latter line. The hydrogen bonding is weak since fairly high concentrations of the H-bonding solvent is required. At one atmosphere of CO_2 , no H-bonding was observed, as is to be expected for such low CO_2 concentrations.

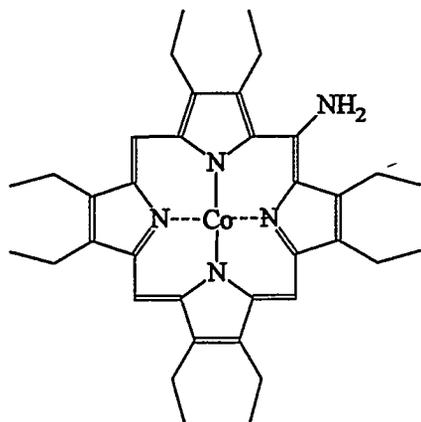
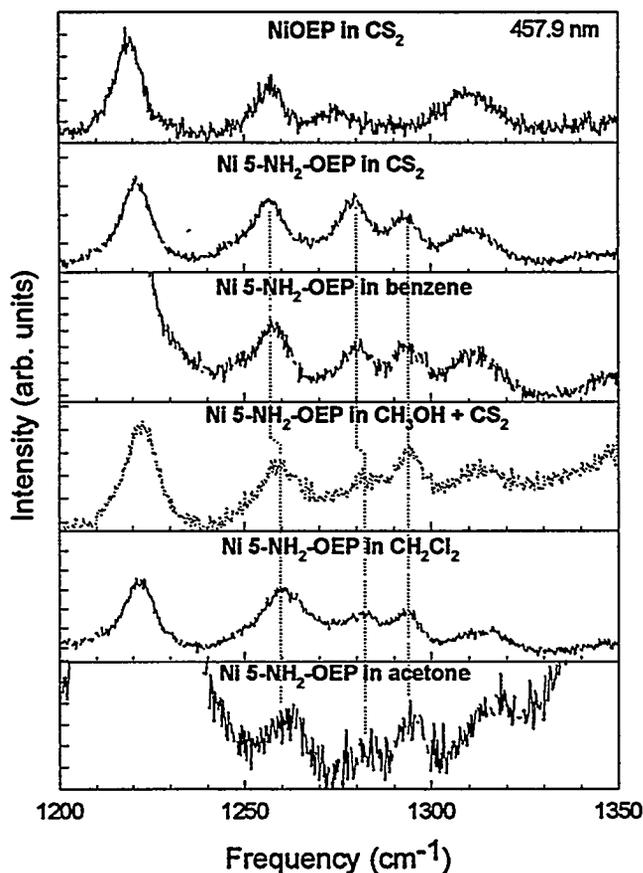


Figure 24. Cobalt 5-amino-octaethylporphyrin. The amino group is an H-bond donor and acceptor.

Figure 25 Resonance Raman spectra of nickel(II) 5-NH₂-OEP (and NiOEP for comparison) in various solvents. This region of the spectrum contains the C-N stretching vibration which normally occurs in the 1260-1330 cm^{-1} range for primary aromatic amines.



Hydrogen bonding to substrates with H-bond donor groups also may have been detected for 5-monoformyl-octaethylporphyrin (5-CHO-OEP). However, in this case the interpretation is complicated by the presence of two conformers—one for which the formyl group is perpendicular to the plane of the porphyrin and another for which the formyl is parallel to the porphyrin ring and conjugated with the ring. These conformers also differ in the degree of nonplanarity, adding further complexity to any interpretation in terms of H-bonding. The metal derivatives of 5-mono-hydroxyethyl-octaethylporphyrin (5-CH₂OH-OEP) have also been synthesized and investigated for H-bonding to donors and acceptors.

Because of these promising results the next step is to synthesize the 5,15-*diamino*-, 5,15-*diformyl*-, and *dihydroxyethyl*-OEP derivatives; molecular modeling suggests much stronger H-bonding to this derivative. At this point, we can say that hydrogen bonding to at least the NH₂ group does occur and probably is strong enough to promote substrate binding and conversion, but not so strong as to interfere with catalytic reactions occurring at the metal site. Synthesis of the

cobalt derivatives of the 5-amino, 5,10-diamino, and 5,15-diamino derivatives in large enough quantities to test in electrochemical CO₂-reduction reactions should be a goal of future research in this area.

We are continuing our efforts aimed at the synthesis of porphyrins with chiral hydrogen-bonding functionality. These catalysts will serve dual purposes as chiral alkane and olefin oxidation catalysts and as CO₂-reduction catalysts, depending on whether Fe or Co are incorporated into the porphyrin. As enantioselective oxidation catalyst the H-bonding functionality gives a stronger interaction with the substrate which can be used to direct the approach of the substrate to the catalytic metal center. The probable result for a H-bonding substrate molecule is higher enantiomeric excesses than can be attained in the absence of H-bonding groups. Synthesis considerations forced us to change our original target catalyst design to that illustrated in Figure 18. The most promising design is now that in which the chiral hydrogen-bonding functionality is attached at one of the *pyrrole*-carbons via the Suzuki reaction. The result is a porphyrin with eight chiral substituents attached. The desired effect of the chiral substituents is to place two hydrogen-bond donor functionalities (the -OH groups shown in Figure 26) in the groove in which CO₂ is bound. There is another advantage of this molecular design over that suggested previously in that the chirality of the cavities on the top and bottom of the porphyrin are identical.

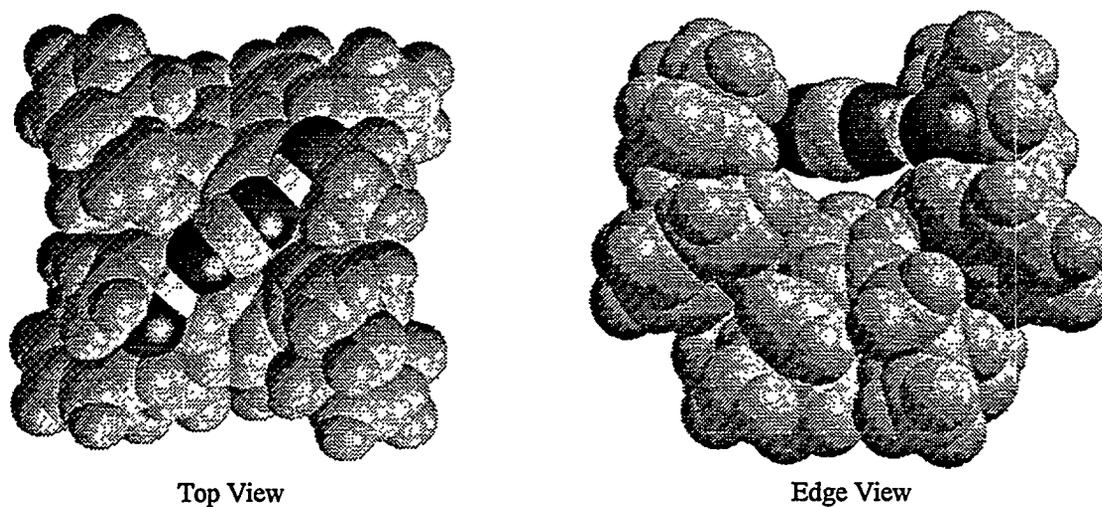


Figure 26 Chiral octasubstituted derivatives of cobalt tetraphenylporphyrin. These catalysts are expected to be active and stable CO₂ reduction catalysts with hydrogen-bonding functionality provided by the OH (or NRH, and NH₂) groups of the chiral substituents (in this case CH₂C^{*}HOHCH₃). For the conformer shown, the OH groups (red and white) are located at each end of the CO₂-binding cavity; CO₂ is red and gray.

¹ "Enhancement of Solar Photocatalytic Detoxification by Adsorption of Porphyrins onto TiO₂" Majumder, S. A.; Prairie, M. R.; Ondrias, M. R.; Shelnut, J. A., *Solar Engineering-Vol. 1*, 1992, Eds. Stine, W.; Kreider, J.; Watanabe, K., ASME: New York, pp. 9-14. SAND91-1856C.

² Furuya, N.; Koide, S. *Electrochimica Acta*, **1991**, *36*, 1309-1313; Ikeda, S.; Ito, T., Azuma, K.; Ito, K.; Noda, H. *Denki Kagaku Oyobi Kogyo Butsuri Kagaku*, **1995**, *63*, 303-309

³ Electrosynthesis Corporation, 72 Ward Rd., Lancaster, NY14086; 4% Co Tetramethoxyphenyl porphyrin gas diffusion electrodes.

DISTRIBUTION:

1	MS 0710	G.N. Ryba, 6210
1	0710	J.A. Shelnut, 6210
1	1407	R. A. Assink, 1811
1	0703	M. Prairie, 6216
1	0188	LDRD Office, 4523
1	9018	Central Technical Files, 8940-2
5	0899	Technical Library, 4414
2	0619	Review & Approval Desk, 12690 For DOE/OSTI