Catalytic Activation
of Carbon Dioxide

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Foreword

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that, in order to save time, the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable, because symposia may embrace both types of presentation.

Preface

INCREASING USE OF FOSSIL FUELS (petroleum, coal, and gas) will continue to load the atmosphere with carbon dioxide beyond the apparent capacity of the plant and oceanic sinks to absorb the gas. There has been an estimated 15% increase in atmospheric carbon dioxide since the turn of the century (*1*). An active response to this worldwide problem is to capture and chemically convert the carbon dioxide at its source of production. Ironically, these conversion processes must be powered by nonfossil fuel sources (solar or nuclear) to achieve a net reduction in atmospheric carbon dioxide.

The expected return of oil price increases over the next decade will again spur investigation into conversion processes for alternative fuel sources such as coal. Coal gasification will produce substantial amounts of carbon dioxide as a by-product. If this carbon dioxide could be converted economically to methanol or methane, established zeolite catalytic processes could convert these intermediates to gasoline. Furthermore, concern about providing a substitute for natural gas to the established gas pipelines has led the Gas Research Institute to sponsor investigation of carbon dioxide conversion selectively to methane (*2*).

This volume is based on a symposium that is part of a continuing series in the Surface Science of Catalysis, sponsored by the Division of Colloid and Surface Chemistry of the American Chemical Society. The symposium was motivated by an interest in C_1 chemistry and the desire to convert an abundant material, carbon dioxide, into useful products.

Investigation of carbon dioxide catalytic activation is explored by a variety of subdisciplines (homogeneous catalysis, heterogeneous catalysis, electrocatalysis/photoelectrocatalysis), often with little cross-citation of work. This situation created a need to bring together the leading researchers to provide an overview of methods and accomplishments to date.

The papers range from general issues (sources, economics, and physical properties) to theoretical treatments of carbon dioxide bonding, followed by the various catalytic approaches (homogeneous, enzymatic, heterogeneous, electrocatalytic, hybrid, photoelectrocatalytic). The volume does not cover noncatalyzed photochemical reactions or energetic particle (electron beam and fission fragment) activation of carbon dioxide. These methods and an overview of earlier approaches for converting carbon dioxide can be found in a series of reports prepared at Brookhaven National Laboratory (*3*).

Realistically, both carbon dioxide and carbon monoxide need to be examined as feedstocks for future appli ttions. These two materials are linked together through the water gas shift reaction:

$$CO + H_2O = CO_2 + H_2$$
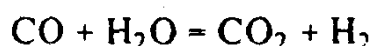
The recent advances in catalysis of the shift reaction have been reviewed by Ford (4), Laine (5), and in a companion volume in the Symposium Series, *Catalytic Activation of Carbon Monoxide* (6).

Prior to this symposium, reviews of homogeneous (7, 8) and electro-catalytic (9) activation of carbon dioxide suggested its emergence as an alternative to carbon monoxide, primarily on the basis of its low cost, abundance, and lower toxicity. The challenge with carbon dioxide reactions (in which hydrogen species act as oxygen acceptors) is to overcome the kinetic barriers to reaction.

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Contents

INDEXES

Chapter 1

Sources and Economics of Carbon Dioxide

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In order for carbon dioxide to be
considered as a significant feedstock for
the chemical industry it must be both
readily avialable and economically
attractive. Sources of carbon dioxide can
be catagorized in terms of the
concentration of this material - high or
low. Examples of the former include
natural reservoirs, natural gas processing
plants and facilities engaged in the
production of ethylene oxide, ammonia or
hydrogen. The largest potential supply of
carbon dioxide, however, is from the
dilute sources which comprise various
fossil fueled power plants (including
coal, oil-and gas-fired facilities).
This paper will discuss some of the issues
associated with the various sources as
well as provide a perspective on their
economics.

Carbon dioxide is an industrial gas with two distinct
identities. Its traditional role relates to recovery from
ammonia production and use in urea manufacture. Smaller
amounts are recovered from other sources (e.g., ethanol
plants), and the merchant CO_2 market also includes
consumption in end uses such as refrigeration and beverage
carbonation. An exciting potential, of course, is for use
as primary petrochemical feedstock.

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Conventional uses for CO_2 are:

1. Urea (approximately 5200 thousand metric tons/year) - this is basically a captive market.
2. Refrigeration (approximately 1500 thousand metric tons/year).
3. Beverages (approximately 750,000 metric tons/year).
4. Enhanced oil recovery (approximately 6-7 million metric tons/year).

As detailed below the basic sources of CO_2 are natural gas processing plants, ethanol plants, ammonia plants, hydrogen plants and ethylene oxide plants. In addition, there are a variety of dilute sources, the largest category of which is power plants. As shown below, of the man-made sources, the largest is ammonia production approximately 1100 MCF (million standard cubic feet). This is to be compared with approximately 80-90,000 MCF from power plants. Natural sources total 1500-2000 MCF. the economics for the use of carbon dioxide arising form these high concentration sources is dependent on clean-up and compression cost.

Natural Reservoirs

The major reservoirs of natural CO_2 occur around the Permian Basin area. Sheep Mountain, in southeastern Colorado is estimated to contain one trillion cubic feet (TCF) of CO_2 of 97% purity. Productive capacity is approximately 300 MCF per day. Other important sources include Brano Dome in New Mexico with reserves of 5 TCF and with total productive capacity of approximately 350 MCF per day. The McElmo Dome has reserves of greater than 8 TCF (97% purity) of the same productive capacity as the Brano Dome Unit. The potential for the McElmo Dome is believed to be approximately 1 billion cubic feet per day. In addition, other units include Jackson Dome, Mississippi (1 TCF proven) and the LaBrage area of southwestern Wyoming which is believed to have reserves in excess of 20 TCF. These data, based on the 1984 National Petroleum Council study of enhanced oil recovery, indicate that the aggregate supply is approximately 2 billion cubic feet per day.

Natural Gas Processing Plants

There are many deposits of natural gas which also contain appreciable quantities of CO_2. The CO_2 can be separated by any one of a number of acid gas removal processes. The approximate CO_2 emission from the natural gas processing plants is given in the table below:

Natural Gas Processing Plants Emitting CO_2

State	Approximate CO_2 Produced (MCF/Day)
Louisiana	6
New Mexico	12
Texas	210
W. Virginia	20
Wyoming	6
Total	254

Source: "Feasibility and Economics of By-Product CO_2 for Enhanced Oil Recovery", DOE contract DE-AT21-78, p.181-182 MC08333.

As is the case for natural CO_2 reservoirs, CO_2 recovered from natural gas processing plants is generally of sufficient quantity to be pipelined to oil fields for use in miscible flood cooperation. Carbon dioxide produced from this source is generally considered to be distinct from traditional merchant market sources.

Ethanol Plants

The sources of ethanol in the United States have been undergoing significant change in recent years. Up until the past few years, synthetic ethanol dominated the industrial ethanol market. Domestic fermentation ethanol capacity for industrial/fuel applications was negligible compared to the capacity for synthetic ethanol.

Over the past five years, the capacity of plants making fermentation ethanol primarily for fuel use has rapidly increased. Fermentation ethanol capacity in the United States is estimated to be approximately 850 million gallons per year.

In the fermentation process, CO_2 and ethanol are produced in roughly equal weights. This translates into a CO_2 production rate of about 60 SCF per gallon of ethanol. Based on the capacity figure cited above, total CO_2 supply from this source is estimated to be 130 MCF/D. Recovered CO_2 from this source would generally find application in the conventional CO_2 merchant market.

Ammonia Plants

Ammonia is produced by the catalytic reaction of nitrogen and hydrogen at high temperature and pressure. The overall process includes the major steps of desulfurization, reduction of feed with steam and reaction of reformed gas with air over catalyst. Subsequently, CO is reformed with additional hydrogen (via steam) and CO_2 is removed.

As a result of the shift reaction, significant quantities of CO_2 are produced during the process, which can be coupled with urea plants to use the CO_2 captively. U.S. ammonia plants have nearly 18 million tons of capacity corresponding to a CO_2 production rate of approximately 1 billion cubic feet per day. This (when subtracted from CO_2 use for urea) translate into an availability of approximately 800 MCF per day. Only about 3.5 million metric tons actually reach the market.

Hydrogen Plants

Hydrogen is produced in large quantities in many refineries for use in operations such as hydrotreating, isomerization and hydrocracking. It is most frequently obtained from a synthesis gas produced by steam reforming of natural gas.

In the production of hydrogen, pressurized natural gas is desulfurized over active carbon or hot zinc oxide, mixed with steam to give the required steam-to-feedstock carbon molar ratio (typically three to one) and then steam-reformed.

To generate a high purity hydrogen product, the CO_2 stream, after moisture removal, is either vented or sold. Approximately 25 SCF of CO_2 are produced for every 100 SCF of hydrogen. At a total U.S. capacity of approximately 2 billion cubic feet per day of hydrogen and approximately 550 MCF per day of CO_2 can be produced.

Ethylene Oxide

The conventional route to ethylene oxide entails the direct vapor phase oxidation of ethylene. The reaction proceeds at 200-300°C and 10-30 atmospheres to produce ethylene oxide in 65-80 mole percent selectivity. The success of this technology is attributable to the development of fairly selective silver oxide catalysts which limit combustion of ethylene to CO, CO_2 and water. The CO_2 is present in the purge gas. Oxygen-based ethylene oxide plants produce approximately 60 MCF of CO_2 per day.

Dilute Sources

Dilute sources of CO_2 consist of sources in which the CO_2 would otherwise be discharged to atmosphere in a flue gas stream. Relatively high expenses would be incurred for recovery of the CO_2.

To date, only one project has attempted to utilize the exhaust stream from an electric power plant for CO_2 recovery. This project involved recovery of CO_2 from the

flue gas of a gas-fired utility boiler and delivered approximately 100 tons CO_2/day.

Coal-fired power plants have CO_2 exhaust content ranging from approximately 23,000 to 43,000 SCF/ton of coal. Oil-and Gas-fired Power Plants, produce approximately 10 billion cubic feet per day.

The estimated total production of CO_2 from power plants is quite large (approximately 90 BCF per day). However, there are a number of issues with respect to the use of such CO_2 including the presence of sulfur compounds in the gas which could seriously effect catalysts.

Summary of CO_2 Supply

Carbon dioxide is derived from natural and man-made sources, with the latter make up of both high concentration and low concentration sources. Of the total CO_2 generated, only a small portion is recovered for subsequent sale, whereas natural CO_2 is generally recovered for large volume applications such as enhanced oil recovery. However, for sheer magnitude, the CO_2 produced in power plants is many times larger than the other sources. Unfortunately, this huge volume of CO_2 is in dilute form necessitating concentration. From the perspective of the chemical industry, as opposed to those interested in the massive use of CO_2 for enhanced oil recovery, the quantities required would appear to be sufficient from the high concentration sources.

Recovery Technology

Carbon dioxide can be recovered in a number of ways. The choice of system depends on various factors, including:

- Feed gas CO_2 concentration and pressure
- Percent recovery required
- Presence of contaminants that may foul the equipment or solvents

Conventional carbon dioxide recovery systems fall into the following categories:

- Chemical solvent systems that chemically react with selected gases, regenerate the solvent by reversing the reaction with heat and/or pressure let down wherein absorbed acid gases are released. The solvents are typically alkanolamines or hot potassium carbonate.

- Physical solvent systems in which gas is absorbed by physical means in a solvent and released by heating and/or pressure let-down.

- Membranes offering the unique property of selective permeability. These are permeable films that permit some gases to transfer through them more rapidly than others, thereby permitting components to be separated. They operate on a continuous flow basis.

- Cryogenic separation in which very low temperatures are used to chill the feed streams and allow distillation of the various components.

Of these alternatives, the solvent absorptions processes are by far the most frequently utilized for CO_2 recovery.

Economics of CO_2 Recovery

Estimation of CO_2 recovery economics is a complex undertaking, primarily because of (a) the wide variations in composition among the many potential feed streams, and (b) the numerous available recovery techniques and configurations thereof.

An important source of CO_2 for recovery is natural CO_2 deposits (e.g., in association with natural gas). Such streams would exhibit a wide range of compositions; one representative stream might be characterized as 50 percent methane and 50 percent CO_2.

The cost of CO_2 recovery from this high level CO_2 stream via a triethanolamine (TEA) solvent process is approximately \$.50/MCF with the major single portion (approximately 45%) being the utility component. For a membrane system the cash cost is lower (approximately \$.40/lb.) with approximately 50% due to uilities. A major difference between the two processes is the relatively high cost of a plant for the former vs. the latter (approximately \$14.2 vs. \$8.4 million for a 6 MCF per year facility) which could increase the net cost of production to approximately \$.64 vs. \$.94 MCF respectively. This analyses suggests that membranes may be an attractive choice for high CO_2 content stream processing.

As noted previously, flue gas is the largest potential source of CO_2. However, recovery costs must be sufficiently low to allow for acceptable end product values. The recovery of CO_2 from flue gases is accomplished with aqueous solutions of MEA. An analysis of the cost of proprietary technologies for recovery of a CO_2 generation plant with a CO_2 recovery capacity of 1000 tons/day reveal a net cost of producing CO_2 to be

approximately \$2.75-3.00/MCF with approximately 1/3 allocated to steam costs.

With both processes, 97 percent of the CO_2 is recovered as product. The methane concentration in the CO_2 product is 3 percent. This reflects a 72.5 percent recovery of methane as a by-product. A second stage of membranes would definitely not be required in this case as it would be in the case of feed streams containing less CO_2.

Summary

Although the dilute sources of carbon dioxide make up the greatest volume of available feed stock, the cost of recovery can be a significant component of the overall cost of a reaction process using such CO_2. As membrane separation processes are further developed, they may become the most cost effective route for recovery and utilization of point source generated carbon dioxide.

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Chapter 2

Carbon Dioxide Equilibria

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The solubility of carbon dioxide in aqueous and non-aqueous solutions depends on its partial pressure (via Henry's law), on temperature (according to its enthalpy of solution) and on acid-base reactions within the solution. In aqueous solutions, the equilibria forming HCO_3^- and $CO_3^=$ depend on pH and ionic strength; the presence of metal ions which form insoluble carbonates may also be a factor. Some speculation is made about reactions in nonaqueous solutions, and how thermodynamic data may be applied to reduction of CO_2 to formic acid, formaldehyde, or methanol by heterogenous catalysis, photoreduction, or electrochemical reduction.

The solubility of carbon dioxide in aqueous or nonaqueous media depends on three primary factors: temperature, partial pressure of carbon dioxide, and acid-base reactions in the solution. Accurate data for solubility and equilibria are well-known for aqueous solutions (1-3), but not for nonaqueous solutions. Neither the standard compilations of equilibrium constants (1,2) nor recent reviews on nonaqueous electrolytes (4) cover what appears to be a large and poorly indexed literature.

The reason I say "poorly indexed" is that out of several thousand entries in the 10th collective index to Chemical Abstracts (1977-81), relating to carbon dioxide, only two entries contained the term "solubility" and neither of these pertained to the solubility of carbon dioxide in a liquid phase. On the other hand, the many entries under terms like "removal from natural gas" implied that quite a lot of data could be found with enough effort.

A historical perspective may give a rough estimate: A compilation reporting work done before 1928 (5), contains three and a half large pages of closely-packed quantitative data for the solubility of carbon dioxide in 48 nonaqueous solvents. A 1958 collection (6) gives 17 pages of tables summarizing the solubility of carbon