

Reductive Sequestration of Carbon Dioxide

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Introduction

The United States currently meets 80% of its energy needs by burning fossil fuels to form CO₂. The combustion-based production of CO₂ has evolved into a major environmental challenge that extends beyond national borders and the issue has become as politically charged as it is technologically demanding. Whereas CO₂ levels in the atmosphere had remained stable over the 10,000 years preceding the industrial revolution, that event initiated rapid growth in CO₂ levels over the past 150 years (Stevens, 2000). The resulting accelerating accumulation of CO₂ in the troposphere is increasingly linked to global climate-warming, with projections of continued warming in the absence of resolute changes in CO₂ management (Revkin, 2000).

The worldwide effects of warming on forestry, fresh water supplies, farming, coastal stability, and human health could be enormous. In response to these threats, the 1997 Kyoto Treaty on Global Warming was initiated in a major world-wide effort to curtail CO₂ emissions. A major feature of this activity involves separation, collection and storage of a significant fraction of the 6-billion tons of CO₂ currently produced worldwide each year. The annual U.S. production is about a third of that value, and sites considered for storing U.S. produced CO₂ include depleted gas reservoirs, deep saline aquifers, depleted oil reservoirs, coal beds, and the deep ocean (Noserale, 1999).

Although accumulating the captured gas in vast reservoirs seems a rational approach to the problem, a second, potentially more rewarding route is suggested here. Because the nominal 2 billion tons of CO₂ the U.S. produces annually represents the energy content of about 11 million barrels of oil per day, or roughly the U.S. daily import (Feld, 2000), we propose that CO₂ be considered a renewable resource. We propose specifically that it be recycled back to fuel by employing water as the hydrogen source, and the reductive chemical energy available from

sunlight driven electron/hole production, or thermal reduction using abundant Fe[II]-containing minerals.

If the process can be successfully applied, it would not only satisfy concerns tied to global warming, but would also eliminate some fraction of the nation's daily dependence on imported oil. This dependence is now a matter of renewed concern and uneasiness with impact on both national security and the economy (Ebel, 2000; New York Times, 2001).

The proposed process involves reductive capture of CO₂ in a two-part scheme related in part to the Fischer Tropsch process, and employing common minerals with sufficient reduction and/or photoreduction potential to convert CO₂ to formate and/or methanol (Yoneyama, 1997) and then to fuel-valued products. Thermochemical calculations show the overall scheme to be highly exothermic, and thus self-sustaining with the proper process design.

Objectives

This paper explores the photochemical and thermochemical parameters associated with reduction of CO₂ to C₁ products and their subsequent conversion to alkanes and proposes a program to assess the key kinetic steps required to effect reduction to methane and higher alkanes. With that information, the overall feasibility of using this process for sequestration of CO₂ can be evaluated relative to other CO₂ sequestration processes.

Background

Carbon dioxide and its aqueous counterparts, bicarbonate and carbonate, are inherently highly stable. Their Gibbs free energies of formation are among the most negative among common molecules (Latimer, 1952), and they are the most stable carbon-containing substances on a per carbon basis at 25°C. The thermochemical gap separating them from organic compounds widens still further at higher temperatures, increasing the difficulty of reducing CO₂ at higher temperatures. It therefore follows that high reduction potentials are required to convert CO₂ and its aqueous ions to organic species. And although such reduction reactions are known, they are presently confined to the use of specialized laboratory reagents and conditions.

Recently, however, the possibility of large-scale, process-level CO₂ reduction has become more viable following two separate published accounts describing the reduction of CO₂ with common minerals. The first is a report by McCollom (2000) who discussed experiments in hydrothermal media with dissolved CO₂ and the mineral olivine, which showed that bicarbonate

ion was immediately reduced to formate at 300°C and 350 bar. These conditions are at pressures above the water saturation curve and therefore there was no headspace in the reactor. McCollom suggested that absence of headspace stopped the reduction at formate, since further reduction to alkanes is highly favored thermodynamically.

McCollom et al. (1999) confirmed this speculation in other work using a system purposefully containing a headspace, in which reduction of aqueous formate to a broad array of hydrogen-rich Fischer Tropsch-like products in the C₂ - C₃₅ range, including alkanes, alkenes, and oxygenated products, readily took place at 175°C. In the absence of headspace, formic acid is in solution, where it is mostly ionized to the stable formate ion. When headspace is available, further reduction occurs in the gas phase through the molecular acid, most probably on the reactor surfaces. Although no elemental balances were provided in the report, it is likely that the conversions proceeded through a series of highly exoergic formic acid disproportionations, like that in Eq. (1) for the formation of alkanes.

These results were in contrast to an earlier account by Berndt et al. (1996) who reported significant conversion of CO₂ to alkanes and aromatics under conditions similar to those of McCollom. However, in additional studies at 300°C with ¹⁴C-labeled bicarbonate, McCollom found only trace quantities of alkanes, which moreover were *unlabeled*. These results showed that the hydrocarbons found by Berndt, et al. must have resulted from contaminants in the mineral, and substantiated the conclusion that with no head space, reduction of CO₂ proceeds no further than formate.



The second account of a mineral-based conversion describes sunlight-driven production of formic acid from CO₂ at ambient temperatures. In this case, Ohta et al. (2000) worked with a selection of common Fe[II]-containing silicate rocks (amphibolite, granite, gneiss, shale) which were powdered and suspended in CO₂-saturated water. When the mixtures were irradiated by sunlight at ambient temperatures, formic acid was formed at a rate of several μgm/m² over 18 hours. No evidence was found for further reduction to other acids or hydrocarbons. Ohta et al. report no effort, however, to identify the specific metal oxide(s) responsible for reduction of CO₂, nor to determine the photoefficiency of the process.

Photoreduction of CO₂ on irradiated semiconductor surfaces has been widely reported to give a range of C₁ and C₂ products, including CO, formate, methanol, methane, formaldehyde, oxalic acid and glyoxal (Yoneyama, 1997). CO₂ photoreductions are observed on a variety of metal oxides, including WO₃, TiO₂, ZnO, as well as on GaP, ZnS and CdS. Reductions are

believed to result from photopromotion of hole/electron pairs in the oxide/sulfide conduction bands, capture of electrons by CO₂ and hole oxidation of water or some added reducing agent. Photoefficiencies for CO₂ reduction appear to range from less than 1% to 23% on certain quantized oxide particles (Yoneyama, 1997; Inoue et al, 1990). The high efficiencies also appear to require large band gaps, thus reducing efficient use of the full spectrum of sunlight.

Approach

The existing literature on CO₂ reductions shows that the reactions do work and can be modified to produce varying proportions of C₁ and C₂ products. However, efficiencies vary widely and the factors controlling selectivity and band gap energies are not well understood. Nor is it clear how the work of Ohta et al. with ferrous minerals relates to the semiconductor oxide processes. Despite these important gaps in understanding these two reduction processes, we propose a scheme to create fuel-valued products from process CO₂, as sketched in Figure 1. The concept effectively utilizes the carbon cycle depicted in the figure to link energy available in the mineral phase (either thermally or photolytically) to that required in the reduction process. The core of the conversion is the central loop in which CO₂ is reduced either thermally or through solar irradiation to formic acid, possibly with conversion of Fe[II] in the mineral feed to Fe[III] in magnetite as the corresponding oxidation. The hydrogen source is water in the feed mixture. In the second step, vapor phase formic acid thermally disproportionates to fuel, which is passed back into the system, and to CO₂, which is returned to the reduction cycle.

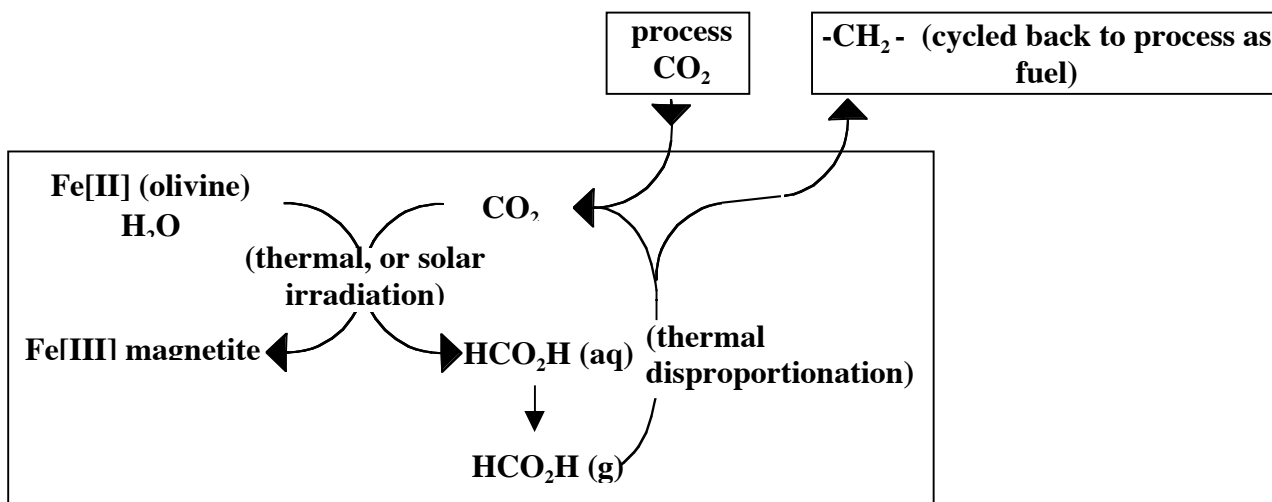
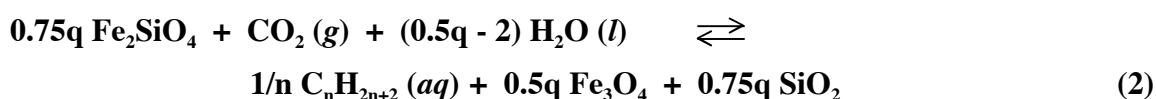


Figure 1. Proposed scheme for the conversion of captured process CO₂ back to fuel-valued products.

Photoreduction of CO₂ to formate using mineral surfaces would be a practical first step for sequestration if: (1) overall photoefficiency were comparable to that of other photoreductions, or about 10-15%; (2) if the active mineral photocatalysts were abundant and easily processed; and (3) if a photoreactor can be designed to efficiently utilize sunlight over a broad range of solar conditions.

The practical features and commercial potential of the conversion scheme can be evaluated by considering the equilibrium positions and reaction heats for the overall conversion of CO₂ to alkanes. Using fayalite (Fe₂SiO₄) as the mineral phase, the stoichiometries are represented by Eq. (2)



where $q = 6 + 2/n$.

Calculations with SUPCRT92 (Johnson et al., 1992) for $n = 1$ to 6 show that the reduction of CO₂ is highly favored, as shown in Figure 2. Methane is the most highly favored alkane, whereas the larger hydrocarbons have log K values more than two orders of magnitude smaller than for methane.

The practicality of the process will ultimately depend upon its thermal and kinetic properties, and in that regard the reaction enthalpies shown for alkane production in Figure 3 are quite encouraging. Conversions of CO₂ are highly exothermic, with the production of methane being the most heat-yielding. Thus, a self-sustaining operation should be attainable with the proper process design.

In summary, it appears that the practical sequestration of CO₂ through conversion to formic acid and fuel-valued materials is feasible. The sensible utilization of the concept will depend on the balance between the fuel value provided by reduction of CO₂ and the energy requirements for reduction. The energy requirements are directly tied to the basic thermochemistry and kinetics of the individual steps in the sequence, including the two thermal and one photochemical step. The program proposed here is designed to develop the necessary kinetic and photochemical parameters to evaluate the commercial potential of CO₂ recycling. Because of the fundamental nature of the study, the results should also serve as a significant contribution to the chemical literature.

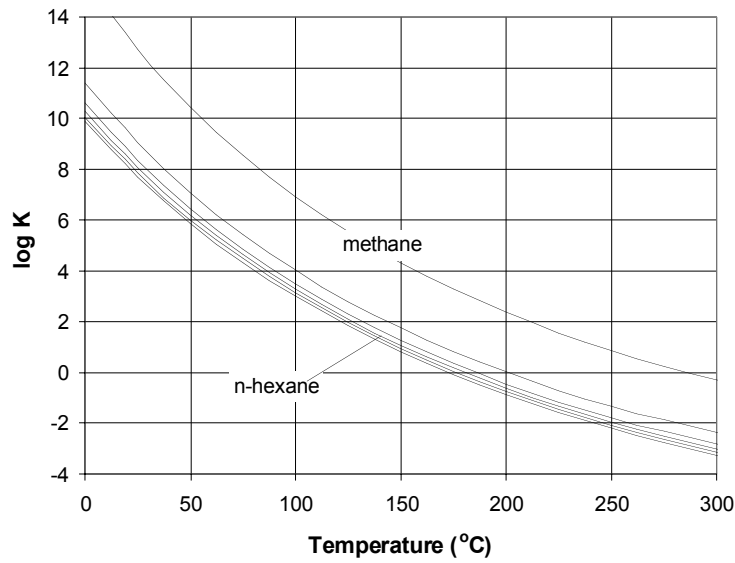


Figure 2. Equilibrium constants for the production of methane through n-hexane via Eq. (2) vs. temperature.

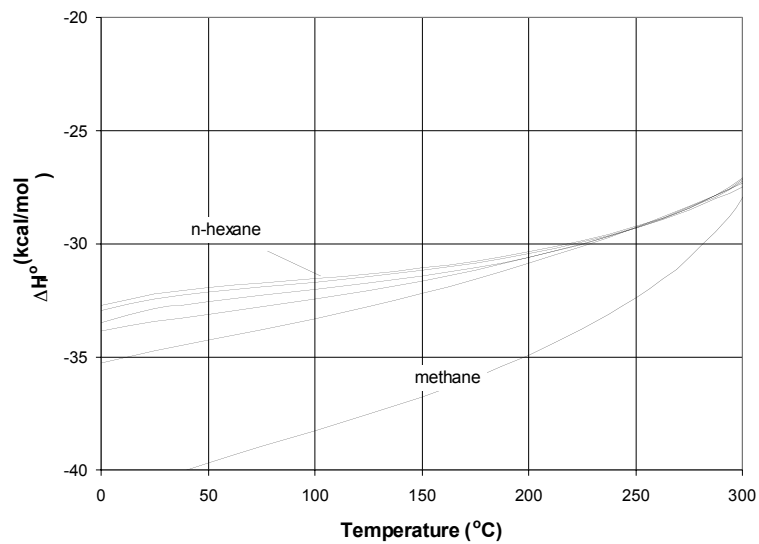


Figure 3. Heats of reaction for the formation of methane through hexane via Eq. (2) vs. temperature. The ordinate values are presented per mole of consumed CO_2 .

Program Description

A research program to evaluate key kinetic and photochemical steps will be conducted over 24 months in which work will be conducted concurrently on the photo- and thermal-reduction processes to allow a direct comparison of their features. Several of the minerals described by Ohta et al. (2000) will be used with near uv light for the initial measurements of CO₂ conversion to formate to confirm their observations. Purified semiconductor oxide components of the minerals will be examined under the same conditions of light intensity, wavelength and particle size to identify the most likely mineral constituents responsible for CO₂ reduction to formate. Band gaps and photoefficiencies of several minerals for reduction of CO₂ will be measured as a function of particle size and the results used to optimize a photoreactor design with practical value. The photooxidation of formic acid back to CO₂ and H₂O will also be examined.

The two thermal steps will be studied in a gold bag reactor designed for hydrothermal studies and product sampling, in order to measure reaction kinetics. For the first step, the effects of pH and temperature on the reduction rates will be determined, and the values of the Arrhenius parameters for the conversion will be determined. In the formic acid thermolysis step, the distribution of products will be examined as a function of reaction conditions and a range of surfaces. The role of headspace and reaction conversion on reaction kinetics and products will be examined in studies over a range of pressures around the vapor/liquid boundary.

The ultimate product of the program will be a detailed understanding of the reaction fundamentals of the multistep process in Figure 1. The database will be suitable for a sound appraisal of the conversion concept, and an evaluation of the prospect of advancing to a process development study.

Authors

Theodore Mill is a senior scientist in the chemistry laboratory at SRI and is an SRI Fellow. He has been involved in environmental and photochemical studies for 30 of the past 40 years at SRI. He led the efforts to develop a quantitative and broad data base of information on chemical reactivity of many kinds of chemicals of concern in the environment including photochemical, hydrolysis and oxidation rates and developed experimental and predictive methods for determining these rates for these chemicals in surface waters.

In addition, he has helped understand the intrinsic photochemical reactivity of natural waters, as characterized by the free radical and other transient oxidation species formed by

sunlight interaction with dissolved organic materials in the water. He has also investigated several kinds of photochemical systems designed to oxidize organic compounds in water, including titania semiconductor-promoted oxidation and reduction.

David Ross recently retired from SRI after 34 years as laboratory chemist, department director, laboratory director and senior scientist. He currently holds positions of associate with the USGS, and adjunct professor in the chemistry and biochemistry department at the State University of California at San Francisco.

During his 34 years at SRI, Dr. Ross conducted research on reaction rates and chemical kinetics in energy- and environmentally-related topics. Evolving from his early studies of petroleum and coal in very hot water, his focus broadened to include a range of subjects bound to the properties of, and reactions in, hydrothermal media. His work has emphasized the phase relationships and the effects of salts in such media in practical application. Recent activities included major government and commercial programs in waste treatment, with a focus on hazardous and toxic waste disposal to avoid incineration.

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