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UTILIZATION FOR MANNED MARS MISSIONS

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ABSTRACT

Utilization of resources available *in situ* is a critical enabling technology for a permanent human presence in space. A permanent presence on Mars, for example, requires a tremendous infrastructure to sustain life under hostile conditions (low oxygen partial pressure, ultraviolet radiation, low temperatures, etc.). As a resource on Mars, atmospheric CO_2 is: (1) abundant, (2) available at all points on the surface, (3) of known presence--requires no precursor mission to verify, (4) chemically simple--requires no precursor missions to verify composition or properties, (5) can be obtained by simple compression, with no requirements of mining or beneficiation equipment operation. This study examines several novel proposals for CO_2 fixation through chemical, photochemical, and photoelectrochemical means. For example, the reduction of CO_2 to hydrocarbons such as acetylene (C_2H_2) can be accomplished with hydrogen. Acetylene has a theoretical vacuum specific impulse of ~ 375 seconds. We also examine potential uses of CO, as obtained or further reduced to carbon, as a reducing agent in metal oxide processing to form metals or metal carbides for use as structural or power materials; the CO_2 can be recycled to generate O_2 and CO.

INTRODUCTION

Utilization of resources available *in situ* is a critical enabling technology for a permanent human presence in space. A permanent presence on Mars, for example, requires a tremendous infrastructure to sustain life under hostile conditions (low oxygen partial pressure,[1] ultraviolet radiation,[2] low temperatures,[3] etc.). Consequently, there have been numerous studies on the most accessible of Martian resources: atmospheric carbon dioxide.[4-9] Atmospheric CO_2 is: abundant (the atmosphere of Mars consists of 95% carbon dioxide,[1] see table 1); available at all points on the surface; of known presence -- requires no precursor mission to verify; chemically simple -- requires no precursor missions to verify composition or properties; and can be obtained by simple compression, with no requirements of mining or beneficiation equipment operation. This study examines several novel proposals for CO_2 fixation through chemical, photochemical, and photoelectrochemical means. The organization is as follows: the introduction highlights proposed systems for carbon dioxide fixation. A discussion of CO_2 chemistry is followed by examples of proposed light-assisted devices. A specific example of chemical fixation, acetylene (C_2H_2) production, is discussed in the context of a cursory mission analysis.

Many studies focus on obtaining oxygen and the various uses for oxygen including life support and fuel; discussion of carbon monoxide, the co-product from CO_2 fixation revolves around its use as a fuel, being oxidized back to CO_2.[8,9] From a feasibility perspective, many studies often focus on the initial placement of very large[6] and mechanically complex[7] systems on Mars. It may prove essential in the initial phase of the exploration and colonization of Mars to employ novel, lightweight photochemically based systems to produce oxygen and reduced carbon. These mechanically simple systems could serve as low-capacity carbon dioxide separation and conversion devices. It is expected that even after they are supplanted by more sophisticated systems[7] in the future, photochemically based systems will be useful backups in case of a malfunction of the "second generation" systems. We also examine potential uses of CO, as obtained or further reduced to carbon, as a reducing agent in metal oxide processing to form metals or metal carbides. The metals and carbides can then be used as structural or power materials, CO_2 can be recycled to generate O_2 and CO.

The reduction of CO_2 to hydrocarbons can be accomplished with hydrogen. This results in producing a large mass of rocket fuel on Mars from a small amount of hydrogen brought from Earth. For ΔV return missions such as manned Mars missions, most of the initial mass required to be placed in low Earth orbit ("IMLEO") is rocket fuel. Of this, a large fraction comprises the fuel for the return trip and the fuel in LEO required to boost the return fuel to Mars. A mission where the return propellant need not be shipped to Mars, would greatly reduce the required mission mass. Thus, production of rocket propellant from available resources is an extremely high-leverage approach to reducing mission mass.

LIGHT-ASSISTED CARBON DIOXIDE FIXATION ON MARS

Background

The goal of this work is to design photochemical and photoelectrochemical systems for the extraterrestrial manufacturing of products required to sustain a human presence on Mars from atmospheric carbon dioxide. The approach involves coupled catalytic cycles to simultaneously produce oxygen and carbon monoxide. Efficient metal catalysts and photocatalysts are to be used for both half-reactions: i) the deoxygenation of CO_2 to CO; and ii) the evolution of O_2. Oxygen can be used for life support or as an oxidizer in a rocket engine. Carbon monoxide can be used for rocket fuel, for the production of other propellants, in CO fuel cells, or for the winning of elemental metals and semimetals from the respective oxides (SiO_2, Al_2O_3, Fe_2O_3, see table 2) for structural and power materials. The project is based upon an integrated approach: synthesis of candidate materials, assessing their reactivity towards CO_2, fabrication of candidate devices and testing these devices in a simulated Martian environment.

The deoxygenation of CO_2 to CO and O_2 is thermally demanding:

$$2\ CO_2\ \rightarrow\ 2\ CO\ +\ O_2\ ;\ \Delta H° = 566\ kJ\ mol^{-1},\ \Delta G° = 514\ kJ\ mol^{-1}. \qquad (1)$$
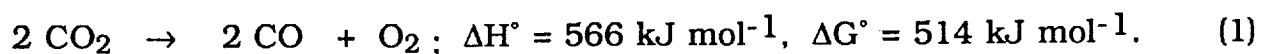
The deoxygenation of CO_2 to CO and O_2 can be effected at temperatures in excess of 1000 K over zirconia,[5] but only by the significant expenditure of a

nonrenewable energy source and at low efficiencies. The solar power density on the surface of Mars is ~250 W m^{-2}, approximately one-fourth that on Earth[10], and more than adequate to power the direct photochemical or photoelectrochemical deoxygenation of CO_2. We propose the development of energy self-sufficient photochemical systems for the production of oxygen and carbon monoxide from carbon dioxide on the surface of Mars.

The deoxygenation of CO_2 to CO and O_2 represents the reverse reaction of the low temperature CO/O_2 fuel cell first devised by Kubiak et al. in 1983:[11]

$$CO + 1/2 \, O_2 \rightarrow CO_2; \qquad \Delta E = 1.33 \text{ V}. \quad (2)$$

Our approach is to drive the endoergic reverse reaction by photochemical and photoelectrochemical electron/hole separation.

The reduction of CO_2 to CO has been studied extensively.[12] The reduction of CO_2 can be accomplished by thermal deoxygenation of CO_2 and O-atom transfer to another substrate:[13,14]

$$^*CO_2 + \text{Sub} \rightarrow \text{Sub=O} + \, ^*CO; \qquad (3)$$
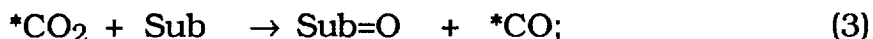
multiple bond metathesis with another unsaturated species:[15]

$$^*CO_2 + C\equiv E \rightarrow O=^*C=E + CO; \qquad (4)$$
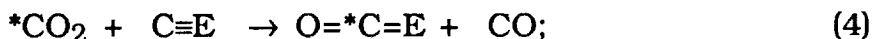
photochemical activation[16]; or electrocatalysis with nickel clusters[17] as shown in figure 1.

Of the various schemes for CO_2 reduction to CO examined to date, the reduction of CO_2 by nickel cluster electrocatalysts[17] holds the greatest promise for a useful device. The proven ability of nickel cluster compounds to electrocatalyze the reduction of CO_2 to CO very near the expected thermodynamic potential will be coupled with photocatalytic and photoelectrochemical systems for oxygen evolution to accomplish the overall "splitting" of CO_2 to CO and O_2.

A necessary component of the photochemical system is the "splitting" of water. The separation of water into H_2 and O_2 is a problem of both tremendous fundamental interest and significant technical difficulty.

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Aqueous solutions of ruthenium bipyridine oxo complexes have been found by Meyer *et al.* to catalyze the "splitting" of water to oxygen.[18] The requirement of an aqueous solvent for the ruthenium catalysts, however, renders them awkward for use on Mars (T ≈ -50° C). Platinum electrodes exhibit the lowest known overpotentials for oxygen evolution and are generally regarded to be the oxygen electrode materials of choice. Recent molecular photochemical studies on platinum hydroxide and related alkoxide complexes suggest that the photochemical elimination of O_2 can be achieved *via* intermediary peroxides.[19] These photochemical reductive eliminations result in the net two-electron reduction of platinum(II) to platinum(0). We propose to couple these photoredox systems and others like them with the known electrocatalytic reduction of CO_2 to CO by nickel clusters.[17] The potentials for platinum(0) reoxidation to platinum(II) match well with the potentials for the electrocatalytic reduction of CO_2 to CO by nickel clusters.[17]

Proposed Devices for Carbon Dioxide Fixation

A proposed $Pt(Ni_3)_2$ molecular assembly for the photochemical splitting of CO_2 to CO and O_2 is presented in figure 2. In the initial step, photoexcitation of the $Pt(OH)_2$ chromophore induces the elimination of oxygen and reduction of Pt(II) to Pt(0). The Pt(0) center is capable of electron transfer to the pendant Ni_3^+ clusters. Each reduced Ni_3 cluster thus formed is known to effect the reduction of CO_2 to CO. After discharge of both the O_2 and CO, the hydroxylated catalyst can be restored by combination of OH⁻ with the Pt(II) center. We note the system is catalytic in H_2O. No exogenous H_2O or aqueous solvent is required; only one mole of H_2O per mole of $Pt(Ni_3)_2$ catalyst is required. Essentially "dry" devices for operation in a Martian environment can be constructed by immobilization of the $Pt(Ni_3)_2(H_2O)$ in an ionic resin or polymer such as Nafion®.

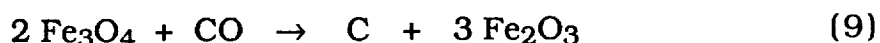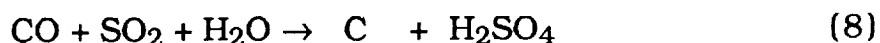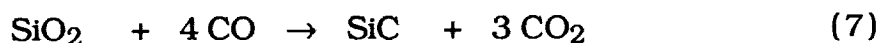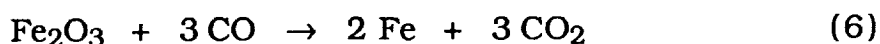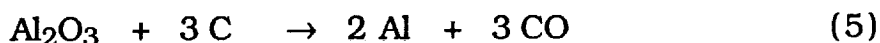Another approach is to prepare solid-state semiconductor photoelectrochemical devices for the splitting of CO_2 to CO and O_2. In particular, p-GaP (E_g = 2.26 eV) has nearly ideal band placement for the photocathodic reduction of Ni_3 cluster electrocatalysts for CO production[17] coupled with anodic oxygen evolution. Irradiation with light above the bandgap of p-GaP should result in the photoreduction of Ni_3 cluster electrocatalysts sites on the surface. These electrocatalytic sites are known

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to reduce CO_2 to CO. The photogenerated holes (h^+) can migrate to the platinized dark side of the device for the reduction of "O^-" ions (which may take the form of O^{2-}, OH^-, HCO^{2-}, or CO_3^{2-} depending on the ionic conductor employed and conditions). A proposed p-GaP device for the splitting of CO_2 is presented in figure 3.

Functioning of such a direct photoelectrochemical reaction on the surface of Mars requires the presence of U.V. photons of energy greater than 2.26 eV. Although the solar spectrum has not been measured at the surface of Mars, the Martian atmosphere, with no ozone layer, apparently allows penetration of solar UV to the surface. The integrated space (AM0) solar spectrum, i.e., total number of photons with energy greater than the photon energy listed, is known for the distance of Earth from the sun.[20] On Mars, the portion of the solar spectrum with $h\upsilon > 2.26$ eV represents an electrolysis current equivalent to roughly 3 mA per cm^2 of solar-exposed surface.

Carbon Monoxide Utilization

Carbon monoxide is a tasteless, odorless, and toxic substance with a melting point of - 205°C (68K) and a boiling point of - 190°C (83K);[21] it is a minor component of the Martian atmosphere, see table 1. As discussed above, carbon monoxide as a resource on Mars, derived from CO_2 fixation, is most often discussed as a fuel.[4,6-9] However, exothermic reaction with O_2 to produce CO_2 is only one potential use for CO. Alternatives take advantage of the reducing chemistry of CO or as a source of carbon.[21-25] Typical examples are highlighted below in reactions (5) - (9) for the potential production of materials useful for structures and power systems.

$$Al_2O_3 \;+\; 3\,C \;\rightarrow\; 2\,Al \;+\; 3\,CO \qquad (5)$$

$$Fe_2O_3 \;+\; 3\,CO \;\rightarrow\; 2\,Fe \;+\; 3\,CO_2 \qquad (6)$$

$$SiO_2 \;+\; 4\,CO \;\rightarrow\; SiC \;+\; 3\,CO_2 \qquad (7)$$

$$CO + SO_2 + H_2O \rightarrow\; C \;+\; H_2SO_4 \qquad (8)$$

$$2\,Fe_3O_4 \;+\; CO \;\rightarrow\; C \;+\; 3\,Fe_2O_3 \qquad (9)$$

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Equation (5) describes a patented process[23] for producing aluminum using carbon and electricity. For each kg of aluminum produced, 3.45 kg of carbon and 32.7 MJ of electrical energy are required. The carbon could be obtained from processes such as (8) or (9) or by electrolysis. Electrical energy could be obtained from solar cells. Equation (6) describes a low temperature reduction of iron oxide that produces iron and carbon dioxide. This system has been studied using mixtures of CO and H_2 as a reductant.[24] Equation (7) summarizes a two-step process for reducing SiO_2 to SiC at temperatures of $1100^\circ C$ under a CO atmosphere.[25] Equations (8) ($25^\circ C$) and (9) ($200^\circ C$) describe relatively low-temperature methods for producing carbon. The sulfuric acid and iron oxide can then be recycled to produce O_2 at elevated temperatures[22] or processed further to produce other materials (i.e. (6) to produce iron). Recycling the products from (8) and (9) results in a process for disproportionating CO into carbon and CO_2. While the practicality of this chemistry has yet to be established, it is important to explore all aspects of CO chemistry to produce as many critical materials from in-situ resources as possible with a minimum of expended energy.

MARS-DERIVED ROCKET FUEL

Background

Tremendous advantages in chemical propulsion missions can be achieved by using Martian resources for propulsion. Mars-derived carbon monoxide can be used directly as a fuel, at a specific impulse of about 300 seconds. For higher specific impulses it is necessary to synthesize hydrocarbon fuels.

Synthesis of methane/oxygen fuels from indigenous Martian materials has been discussed by Ash[4] and others. A Mars mission involving processing of methane fuel is detailed by Zubrin and Baker.[26] Their proposal was for an unmanned preliminary mission to bring to Mars: (1) the return spacecraft, (2) a quantity of liquid hydrogen, and (3) an atmospheric processing module, followed two years later by a manned mission. The processing module processes the hydrogen along with atmospheric carbon dioxide into methane and oxygen by the reaction:

$$4 H_2 + CO_2 \rightarrow 2 H_2O + CH_4. \qquad (10)$$
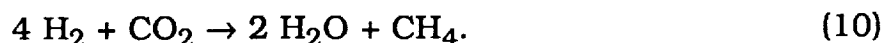
This is a highly exothermic reaction, the rate of which will be limited primarily by the ability to remove the heat produced. The evolved water is recycled to hydrogen and oxygen by electrolysis. Additional oxygen is produced by reduction of carbon dioxide as discussed in the previous section and by other authors.[7,26,27]

The purpose of this chemistry is to produce a large amount of return fuel from a small amount of hydrogen. The required hydrogen is about 5% of the mass of the fuel produced. Another advantage is the ease of storage. Hydrogen brought from Earth is converted into methane and water by reaction (10) within the two days of arrival on Mars, thus eliminating the significant difficulties of long-term cryogenic storage of hydrogen. The Baker/Zubrin proposal envisioned completion of propellant manufacture, resulting in a fully fueled return vehicle on Mars before the manned crew is launched, and contained several safeguards to ensure that the manned crew would reach the fueled return vehicle despite any credible worst-case.

Hydrocarbon Rocket Fuels

If carbon dioxide is the only resource assumed to be used from Mars, then production of hydrocarbon fuels requires hydrogen brought from Earth. It is desirable, then, to maximize the total impulse of fuel produced and minimize the amount of hydrogen required. Thus, it is optimal to utilize a fuel with a minimum hydrogen content. We can define the *propellant mass leverage* as the mass of propellant produced divided by the mass of earth derived components (in this case, hydrogen). The propellant mass leverage of several fuels (for stoichiometric combustion) is shown in table 3.

It is important to note that the mass leverage is not the only factor to be considered in a figure of merit; the specific impulse (I_{sp}) is also quite important, since it determines the amount of fuel required. Hydrogen/oxygen can produce a specific impulse of up to 500; the hydrocarbon fuels about 375, the alcohols slightly less, and carbon monoxide about 300. Carbon monoxide contains no Earth-derived hydrogen, and so has a hydrogen leverage of infinity, but has low specific impulse.

Since stoichiometric hydrogen/oxygen fuel is nearly 90% oxygen by mass, a mass leverage of a factor of nine can be achieved simply by using oxygen derived from carbon dioxide reduction as the oxidizer for Earth-derived hydrogen. A difficulty of liquid hydrogen as a fuel is that it is

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extremely difficult to store. An additional increase by a factor of two in propellant leverage is obtained by use of Mars-derived methane, as shown in (10) above. Use of higher carbon hydrocarbons will gain additional leverage.

Once carbon monoxide is produced on Mars, further synthesis by use of Fischer-Tropsch type reactions can be used to produce alcohols and higher hydrocarbons, as shown in table 4. This synthesis route can be used to produce almost any organic compound of interest, including hydrocarbon fuels, polymers, and processing feedstock for further use.

The alcohol fuels are a special case. The energy content of alcohols is lower than that of the corresponding hydrocarbons, and thus they have a lower specific impulse. The advantage of alcohols is the great ease of storage. With melting points of -97° C and -115° C respectively, methanol and ethanol are liquid over nearly the entire Mars temperature range. Once CO has been produced by the reactions discussed previously, methanol can be produced with high selectivity by catalytic hydrogenation:[28]

$$CO + 2H_2 \rightarrow CH_3OH. \tag{11}$$

This reaction is currently done on a production scale, with a world production on the order of 15 Mtons/yr. Alternatively, methanol can be produced directly from carbon dioxide:[28]

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O. \tag{12}$$

This reaction is less exothermic than the CO reaction, but removal of water from methanol requires an additional step. Ethanol (and higher alcohols) can be produced by Fischer-Tropsch chemistry,[28] although with lower selectivity.

Additional gains in propellant leverage can be obtained by synthesis of higher hydrocarbons. Ethane and ethylene produce only modest improvements over methane. Of hydrocarbon fuels, the minimum hydrogen content fuel is acetylene (C_2H_2, H-C≡C-H). Despite the higher exhaust molecular weight, acetylene has a theoretical vacuum specific impulse slightly better than that of methane. Depending on chamber pressure and area ratio, the specific impulse can be up to about 425 seconds. This is because the higher exhaust molecular weight is offset by the energy content

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of the triple bond, resulting in a high combustion temperature. We assume 400 seconds here. Acetylene is a gas at room temperature, but has a boiling point of ~ -80°C (assuming appropriate pressure to maintain liquid phase), making it even easier to store than methane, which boils at ~ -165°C. While acetylene is thermodynamically unstable, decomposition is not a problem for liquid acetylene stored at low temperature[29]. Acetylene can be produced by thermal or electric arc pyrolysis of methane at around 1250°C[29]:

$$2 \ CH_4 + 184,000 \ kJ \rightarrow C_2H_2 + 3 \ H_2. \tag{13}$$
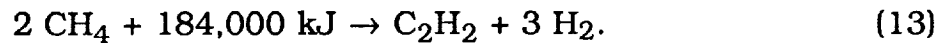
A standard production sequence for acetylene is the partial oxidation of methane, where combustion of the methane with oxygen provides the energy required for pyrolysis:[30]

$$6 \ CH_4 + O_2 \rightarrow 2 \ C_2H_2 + 2 \ CO + 10 \ H_2. \tag{14}$$

This is an industrial reaction sequence which is well developed. The hydrogen can be recycled to methane and reused in reaction (10). Use of acetylene instead of methane decreases the requirement for hydrogen by another factor of four at no reduction in specific impulse. The high flame temperature of the oxygen-acetylene flame will require some development of rocket engine technology. An alternative possibility is to reduce the flame temperature by adding an additional component into the fuel mixture.

One attractive possibility is using as fuel a mixture of C_2H_2 and CO. Since CO is formed as a byproduct of the reactions used to produce acetylene, no additional chemical technology would be necessary. Burned with oxygen, CO produces a theoretical specific impulse of ~300 sec.,[27] depending on the assumed combustion.

A mixture of fuels will produce a composite specific impulse equal to the RMS average of the individual specific impulses, weighted by mass. Thus, an equal mass mixture of acetylene and CO would produce a theoretical specific impulse of about 350 sec. This represents some penalty in I_{sp} over the 400 sec. of acetylene/oxygen alone, but the mixture has only half the requirement for hydrogen brought from Earth, and a much lower flame temperature. The leverage of hydrogen is very large: less than 1% of the fuel mass is Earth-derived hydrogen.

ΔV from the surface of Mars to a Mars-Earth transfer orbit is about 5.7 km/sec on the average. At an I_{sp} of 400, a maximum of 23% of the rocket mass can be injected into the transfer orbit. For the CO/acetylene mixture I_{sp} of 350, this is reduced to 18%. While a large fraction of this may be tank weight, it still is likely that the reduction in mass fraction due to lower I_{sp} is more than compensated for by the decrease in requirement of Earth-derived hydrogen.

With such high leverage of hydrogen, it becomes possible to consider use of Mars sources of hydrogen. Water is believed to be present in the form of permafrost beneath the surface and in the form of water ice in the polar caps.[31] Use of such a resource, however, would require both precursor missions to locate the resource, and mining and refining equipment to dig out and purify the water. The Viking orbiter mapped the water vapor content of the Martian atmosphere[1] and as a result we now know the atmosphere to be nearly saturated with water vapor, about 0.03% composition by volume, varying with location and season. This results in an amount of precipitable water between 1 and 100 microns.[31,32] Water can be precipitated out of the Martian atmosphere by either of two relatively simple mechanical processes: adiabatic expansion,[33] or isothermal compression.[34] Water could be produced from the atmosphere at a rate on the order of one kilogram per 10^6 m^3 of atmosphere processed. This water could then be electrolyzed to produce the hydrogen required for fuel production, and oxygen. The amount of oxygen produced would be sufficient to eliminate the need for reaction (1) above, assuming a stoichiometric fuel ratio. In this case, no reactants need be brought from Earth at all for fuel production on Mars.

Effect on Mission Mass

One figure of merit for savings is initial mass in low Earth orbit, IMLEO. Clearly, mission mass savings will depend on the details of the mission architecture, including such details as use of aerobraking and aerodynamic decelerators, whether a Venus swingby is used, whether a habitat is placed in high or low Mars orbit, etc.

A rough figure of merit can be calculated from the required orbital ΔV. Average ΔV needed to go from low Earth orbit to trans-Mars injection (Hohmann transfer) is 4.3 km/sec (the actual value will depend on the

mission year, since the orbit of Mars is significantly eccentric). The average return ΔV from the surface of Mars to trans-Earth injection is 5.68 km/sec. The mass ratio, or total fueled vehicle mass over final mass, is exponential in the mission ΔV:

$$M_i/M_f = \exp{(\Delta V/gI_{sp})}. \qquad (15)$$

Under the most optimistic assumptions, assuming aerobraking at Mars and Earth arrival at no cost in added mass, an I_{sp} of 450 sec (LH_2/LOX), and no allowances for fuel tank mass and engines, every ton of mass injected from Mars to Earth requires 2.6 tons of fuel on Mars. Shipping this fuel to Mars would require an additional 4.3 tons of fuel in LEO. Manufacturing return fuel on Mars will thus reduce the IMLEO by nearly a factor of seven. More pessimistic assumptions adding weight for tanks, aerobrake mass, etc, will increase the advantage of Mars-manufactured propellant even further. Lower values of I_{sp}, as would be required for space-storable propellants, will also increase this factor, while habitats or vehicle mass left in Mars orbit or left behind on the surface will decrease the factor. In any case, however, manufacturing fuel from in-situ resources on Mars results in huge savings in mass.

CONCLUSIONS

We propose a novel chemical approach to *in situ* resource utilization for manned Mars missions. Carbon dioxide fixation can not only be carried out using purely chemical means but also by taking advantage of another accessible Martian resource, ultraviolet photons. The proposed light-assisted carbon dioxide fixation chemistry has the potential to produce lightweight, mechanically simple devices for oxygen production. It is anticipated that the invention of new devices and systems studies will result in an enhanced understanding of photochemical applications for *in situ* resource utilization. A parallel study of carbon monoxide as a reductant in processing native oxides on Mars is underway. Novel processes involving carbon monoxide in metal and semimetal oxide reduction may enhance the value of the products of carbon dioxide fixation and conserve hydrogen for other uses.

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Relatively simple and well-understood chemical reactions can be used to produce hydrocarbon rocket fuels on Mars from hydrogen. Use of such a process allows an amount of fuel to be produced on Mars which is nearly 100 times the mass of hydrogen brought from Earth. If such a process produces the return propellant for a manned Mars mission the required mission mass in LEO is reduced significantly over a system using all Earth-derived propellants. A further decrease in the requirement for Earth-derived hydrogen is found if the carbon monoxide produced as a by-product of acetylene production is also used as a fuel component. Propellant brought from Earth could be entirely eliminated if a convenient source of hydrogen on Mars such as atmospheric water could be used. Even the simplest processing sequence, manufacturing oxygen, would reduce fuel requirements on Mars by a factor of four if CH_4 propellant is brought entirely from Earth.

If only one single idea is to be emphasized, it is that the carbon dioxide atmosphere of Mars is a significant, abundant resource for manufacturing critical materials on Mars. There are many possible chemical sequences to utilize the CO_2 and reduced by-products CO and carbon. The processes discussed for making hydrocarbons and alcohols from CO_2 and reducing metal oxides with CO and carbon are thermodynamically feasible but may not be practical. There are likely to be other sequences that are more useful. At this stage in the definition of manned Mars missions, it is important to explore the full range of the known chemistries of simple carbon compounds. A more thorough exploitation of easy-to-obtain resources will enhance the potential for *in situ* resource utilization. Further progress in simplifying *in situ* manufacturing technology will provide for lighter, less-expensive missions and increase the likelihood of manned planetary exploration in our lifetime.

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REFERENCES

[1] Meyer, T.R. and McKay, C.P., *J. Brit. Interplan. Soc.* **42**, 147 (1989).

[2] Oro, J. and Holzer, G., "The effects of ultraviolet light on the degradation of organic compounds - A possible explanation for the absence of organic matter on Mars", in *Life Sciences and Space Research XVII: Proceedings of the Open Meeting of the Working Group on Space Biology*, Pergamon Press: Oxford, U.K., 1979, pg. 77.

[3] Jakosky, B.M. and Haberle, R.M., *J. Geophys. Res.* **95**, 1359 (1990).

[4] Ash, R.L., Dowler, W.L. and Varsi, G., *Acta Astronautica* **5**, 705 (1978).

[5] Richter, R., "Basic Investigation into the Production of Oxygen in a Solid Electrolyte Process", in *AIAA 16th Thermophysics Conference*, Palo Alto, CA, AIAA Paper 81-1175, June 1981.

[6] Johnson, S.W. and Leonard, R.S., "Manned Mars Missions and Extra-terrestrial Resource Engineering Test and Evaluation," AAS Paper 87-263, in *The Case for Mars III: Strategies for Exploration - Technical*, Univelt, Inc.: San Diego, CA, 1989, pg. 455.

[7] Ash, R.L.; Werne, J.A., and Haywood, M.B., "Design of a Mars Oxygen Processor", AAS Paper 87-263, in *The Case for Mars III: Strategies for Exploration - Technical*, Univelt, Inc.: San Diego, CA, 1989, pg. 479.

[8] Galecki, D.L., "In-Situ Propellant Advantages for Fast Transfer to Mars," in *AIAA/ASME/SAE/ASEE 24th Joint Propulsion Conference*, Boston, MA, AIAA Paper 88-2901, July 1988.

[9] Frisbee, R.H., "Mass and Power Estimates for Mars In-Situ Propellant Production Systems," AIAA Paper 87-1900, June 1987.

[10] Appelbaum, J., and Flood, D.J. *"Solar Radiation on Mars, Update 1990,"* NASA Technical Memorandum 103623, Oct. 1990.

[11] Wu, J. and Kubiak, C. P., *J. Am. Chem. Soc.* **105**, 7456 (1983).

[12] Darensbourg, D.J. and Kudaroski, R.A., *Adv. Organomet. Chem.* **22**, 129 (1983).

[13] Wu, J., Fanwick, P. E. and Kubiak, C. P., *Organometallics* **6**, 1805 (1987).

[14] Bryan, J. C.; Geib, S. J.; Rheingold, A. L; and Mayer, J. M., *J. Am. Chem. Soc.* **109**, 2826 (1987).

[15] DeLaet, D. L., del Rosario, R., Fanwick, P. E. and Kubiak, C. P., *J. Am. Chem. Soc.* **109** , 754 (1987).

[16] DeLaet, D. L., Lemke, F. R. Gao, J. and Kubiak, C. P., *J. Am. Chem. Soc.* **110**, 6904 (1988).

[17] Ratliff. K. S. and Kubiak, C. P., *Organometallics*, in press.

[18] Gilbert, J. A., Eggleston, D. S., Murphy, W. R., Jr., Geselowitz, D. A., Gersten, S. W., Hodgson, D. J. and Meyer, T. J., *J. Am. Chem. Soc.* **107**, 3855 (1985).

[19] Ni, J., Fanwick, P. E. and Kubiak, C. P., *J. Am. Chem. Soc.*, in press.

[20] "Solar Constant and Air Mass Zero Solar Spectral Irradiance Tables," ASTM Standard E490-73a (Reapproved 1981), ASTM: Philadelphia, PA, 1985, pg. 428.

[21] F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry, Fifth Edition*, John Wiley and Sons: New York, 1988.

[22] Martin, L.R. and Webb, H.M., "Transportable Fuels Via A Carbon Resource Recovery Technique," in *AIAA/ASERC Conference on Solar Energy: Technology Status*, Phoenix, AZ, AIAA Paper 78-1780, November 1978.

[23] U.S. Patent 4,299,619, issued 1981.

[24] Hughes, R., Kam, E.K.T., and Magadam-Zadeh, H., *Thermochimica Acta* **59**, 361 (1982).

[25] Japanese Patent 62 72,113, issued 1985.

[26] Zubrin, R. and Baker, D., "Humans to Mars in 1999," *Case for Mars Conference IV*, Boulder, CO, June 1990; also Baker, D., and Zubrin, R., *J. Brit. Interplanetary. Soc.* **43**, 519 (1990).

[27] Clapp, W.M. and Scardera, M.P., "Applications of In-Situ Carbon Monoxide-Oxygen Propellant Production at Mars," AAS Paper 87-212, in *The Case for Mars III: Strategies for Exploration - Technical*, Univelt, Inc.: San Diego, CA, 1989.

[28] Sneeden, R.P.A., in *Comprehensive Organometallic Chemistry*, Vol. 8, G. Wilkinson, F.G.A. Stone and E.W. Abel, eds. Pergamon Press: Oxford, U.K., 1982, pg. 1.

[29] "Acetylene," *Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, volume 1*, John Wiley and Sons, New York, 1973, pp. 192-237.

15

[30] Morrison, R.T. and Boyd, R.N., *Organic Chemistry, Third Edition,* Allyn and Bacon, Inc.: Boston, MA, 1973, p. 252.

[31] Duke, M.B., "Mars Resources," *Manned Mars Missions, Working Group Papers,* Vol. 2, NASA M-002, June 1986.

[32] Kaplan, D., *Environment of Mars 1988,* NASA Technical Memorandum 100470, Johnson Space Center, 1988.

[33] Jones, D., "Isentropic Processing for In-Situ Propellant Production on Mars, *Case for Mars Conference IV,* Boulder, CO, June 1990.

[34] Meyer, T.R., Brown, L., and Tarantino, J., "Atmospheric Water on Mars: Energy Extraction Estimates", *Case for Mars Conference IV,* Boulder, CO, June 1990.

TABLE 1.
COMPOSITION OF MARTIAN LOWER ATMOSPHERE*

GAS		PERCENT VOLUME
Carbon Dioxide	(CO_2)	95.32
Nitrogen	(N_2)	2.7
Argon	(Ar)	1.6
Oxygen	(O_2)	0.13
Carbon Monoxide	(CO)	0.07
Water Vapor	(H_2O)	0.03

* - **Source: NASA Technical Memorandum 82478.**

TABLE 2.
APPROXIMATE ELEMENTAL COMPOSITION
AND CHEMISTRY OF VIKING 1 LANDER SITE*

ELEMENTS	PERCENT	COMPOUND	PERCENT
Oxides of H, C, N, Na	40	SiO_2	40
Si	21	Fe_2O_3	18
Fe	13	MgO	8
Unknown	9	SO_3	8
Mg	5	Al_2O_3	6
Ca	4	CaO	6
S	3	TiO_2	1
Ti	1	K_2O	0.3
Sr, Y, K, Zr, Rb (total)	1		

* - Source: NASA Technical Memorandum 82478.

TABLE 3.
IN-SITU PROPELLANT MASS LEVERAGE*

FUEL	REACTION STOICHIOMETRY		LEVERAGE
Hydrogen (Baseline)	H_2	$+ \ 1/2 \ O_2$ (Earth)	1
Hydrogen	H_2	$+ \ 1/2 \ O_2$ (Mars)	9
Methane	CH_4	$+ \ 2 \ O_2$	20
Ethane	C_2H_6	$+ \ 7/2 \ O_2$	24
Ethylene	C_2H_4	$+ \ 3 \ O_2$	31
Acetylene	C_2H_2	$+ \ 5/2 \ O_2$	53
Methanol	CH_3OH	$+ \ 3/2 \ O_2$	20
Ethanol	C_2H_5OH	$+ \ 3 \ O_2$	24
Carbon monoxide	CO	$+ \ 1/2 \ O_2$	∞

* - See discussion in text.

TABLE 4.
THERMODYNAMIC VALUES FOR CO/H$_2$ REACTIONS*

PRODUCT	REACTION	ΔH (kJ mol^{-1})
Methane	$CO + 3 H_2 \rightarrow CH_4 + H_2O$	-206
	$2 CO + 2 H_2 \rightarrow CH_4 + CO_2$	-248
Alkanes	$CO + 2 H_2 \rightarrow (-CH_2-) + H_2O$	-165
	$2 CO + H_2 \rightarrow (-CH_2-) + CO_2$	-207
	$3 CO + 2 H_2O \rightarrow (-CH_2-) + 2 CO_2$	-249
Methanol	$CO + 2 H_2 \rightarrow CH_3OH$	- 90.8
Alcohols	$n CO + 2n H_2 \rightarrow C_nH_{2n+1}OH + (n-1) H_2O$	-124.8

* - **Adapted from text reference [28].**
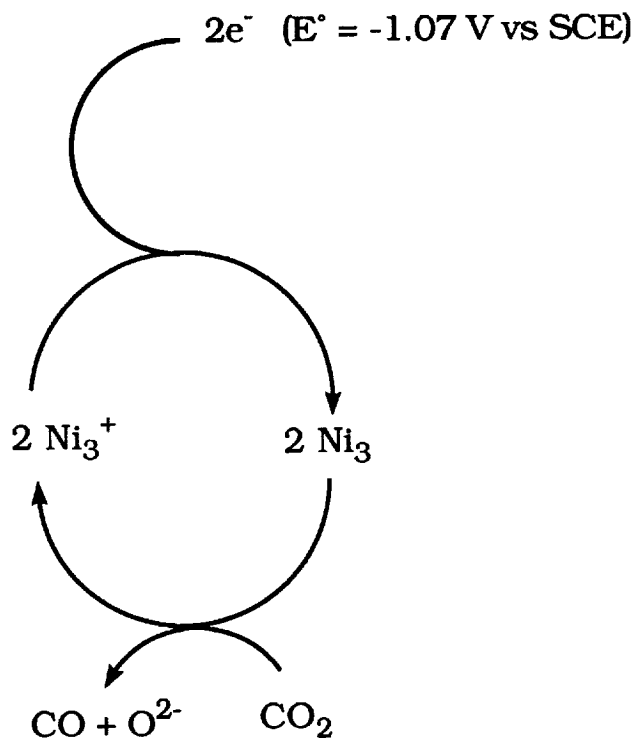
Figure 1. Electrocatalytic splitting of carbon dioxide using nickel cluster catalyst. See text for discussion.

Photoexcitation of Hydroxylated Catalyst
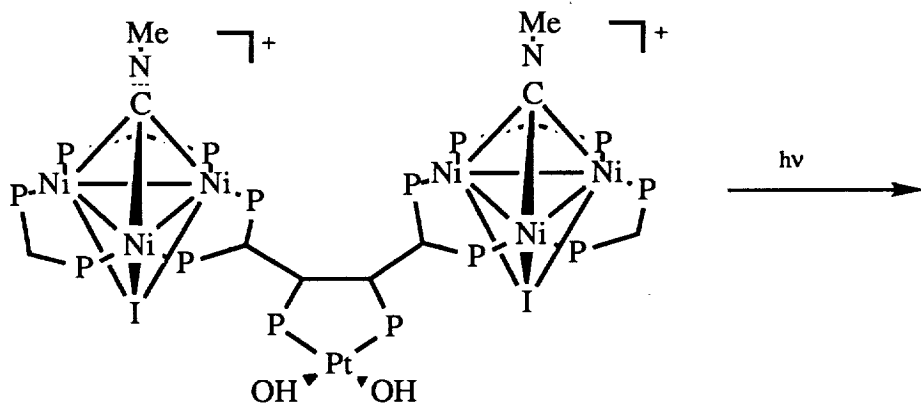
Photoelimination of O₂
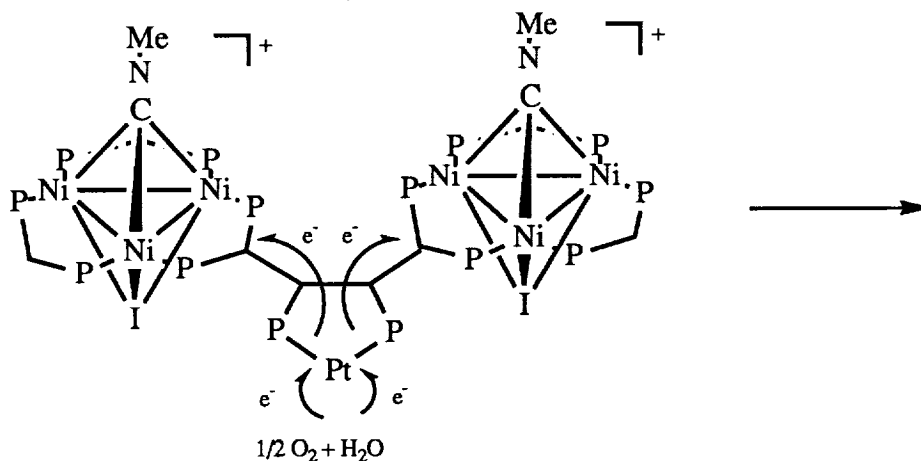
Reduction of CO₂ to CO, Regeneration of Hydroxylated Catalyst

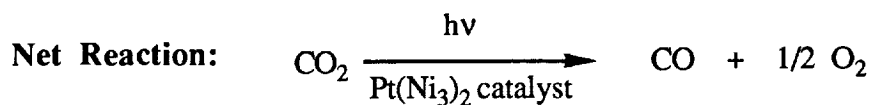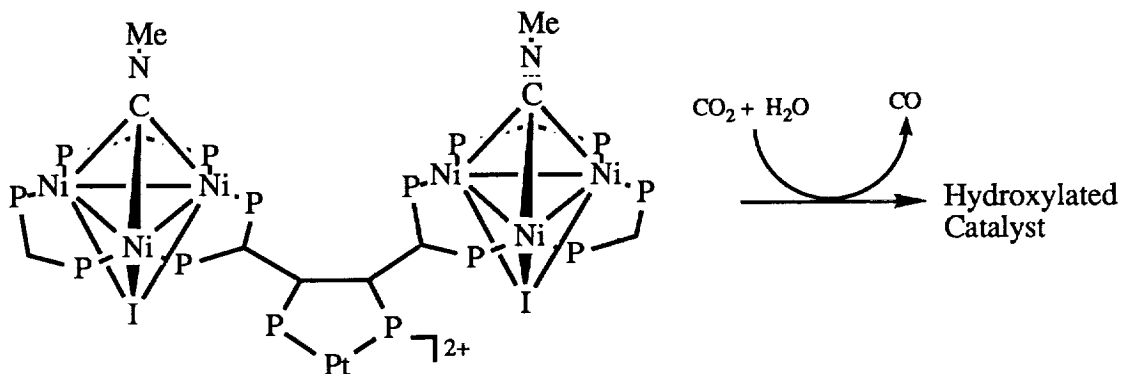Net Reaction: $CO_2 \xrightarrow[\text{Pt(Ni}_3)_2\text{ catalyst}]{h\nu} CO + 1/2\ O_2$

Figure 2. A photochemical system for splitting carbon dioxide. Note that the reaction is also catalytic in H_2O. The reaction produces as much water as is consumed. Added or exogenous water is not required.
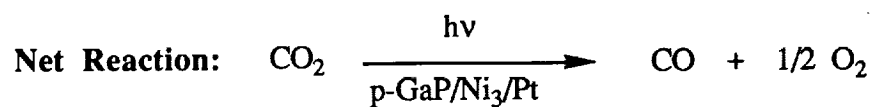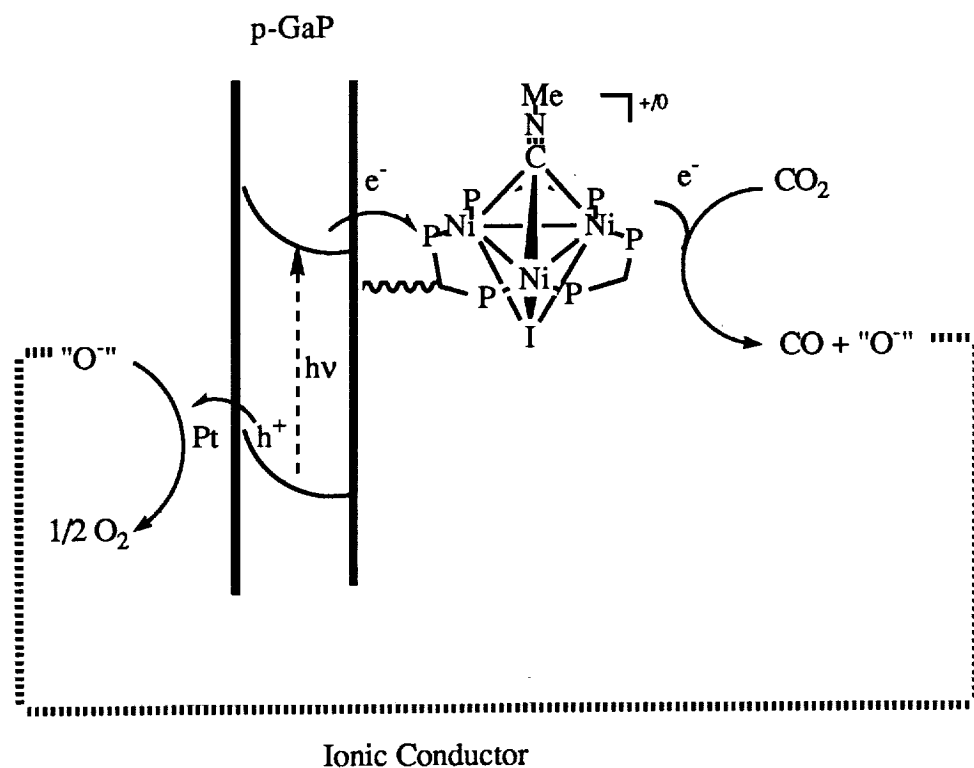
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Figure 3. A semiconductor photoelectrochemical system for splitting carbon dioxide. See text for discussion regarding energy requirement of absorbed photon.

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16. Abstract

Utilization of resources available in situ is a critical enabling technology for a permanent human presence in space. A permanent presence on Mars, for example, requires a tremendous infrastructure to sustain life under hostile conditions (low oxygen partial pressure, ultraviolet radiation, low temperatures, etc.). As a resource on Mars, atmospheric CO_2 is: (1) abundant, (2) available at all points on the surface, (3) of known presence—requires no precursor mission to verify, (4) chemically simple—requires no precursor missions to verify composition or properties, (5) can be obtained by simple compression, with no requirements of mining or beneficiation equipment operation. Many studies focus on obtaining oxygen and the various uses for oxygen including life support and fuel; discussion of carbon monoxide, the co-product from CO_2 fixation revolves around its use as a fuel, being oxidized back to CO_2. This study examines several novel proposals for CO_2 fixation through chemical, photochemical, and photoelectrochemical means. For example, the reduction of CO_2 to hydrocarbons such as acetylene (C_2H_2) can be accomplished with hydrogen. Acetylene has a theoretical vacuum specific impulse of ~375 seconds. We also examine potential uses of CO, as obtained or further reduced to carbon, as a reducing agent in metal oxide processing to form metals or metal carbides for use as structural or power materials; the CO_2 can be recycled to generate O_2 and CO.

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