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Publication Date
1978-10-01
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October 3, 1978

Prepared for the U. S. Department of Energy under Contract W-7405-ENG-48

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Photoassisted Reactions by the Pt-SrTiO$_3$ Single Crystal Sandwich.

The Adsorption of Gaseous H$_2$O and CO$_2$ and the Production of CH$_4$ at the Solid-Gas Interface.

by

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This work was supported by the Division of Materials Sciences
Office of Basic Energy Sciences, U.S. Department of Energy

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Abstract

We report on the photochemical production of CH$_4$ from gaseous CO$_2$ and H$_2$O in contact with a sample consisting of a SrTiO$_3$(lll) single crystal in contact with Pt foil. Radiation with energy greater than the SrTiO$_3$ band gap is effective in photoassisting the reaction. The reaction was studied at total gas pressures of ~30 torr and 300°K and as a function of temperature.

Ultraviolet Photoemission Spectroscopy and Electron Energy Loss Spectroscopy have been used to study the chemisorption of H$_2$O, CO$_2$, O$_2$ and CO on SrTiO$_3$ single crystals. The results of these studies shed light on the mechanism of the methane production photoreaction.
Introduction

There are only a few widely utilized catalytic reactions that are thermodynamically "uphill," i.e., accompanied by a large positive free energy change, but they are of great importance. One is photosynthesis that produces hydrocarbons and oxygen from carbon dioxide and water, and light provides the external energy source necessary for its completion. The other, the electrolytic dissociation of water to hydrogen and oxygen, utilizes an external potential as a source of energy to carry out the electrode reactions. Recently, there have been successful attempts to dissociate water in an electrochemical cell by using light instead of an external potential. Oxygen evolves at the oxide (SrTiO₃, TiO₂) anode and hydrogen at the cathode (Pt or p-type GaP) from a basic aqueous electrolyte solution when light of band gap energy (about 3 eV) illuminates the anode. This photoassisted reaction seems to take place even if the anode and cathode are short circuited, i.e., touching each other. (1-5)

We have embarked on a program to explore the possibility of producing small hydrocarbon molecules from CO₂ and H₂O, at the solid-vapor interface, with the assistance of light. Light, as an energy source, may be utilized to creat electron-hole pairs by direct excitation across the band gap of an insulator or semiconductor, or it may be used for direct excitation of the reactant molecules. We convert light to electron-hole pairs in the excited solid similar to the way it is utilized in the photographic process. The charge carriers must then be trapped by the reactants before recombination occurs. Instead of using the excited charge carriers for a solid state reaction leading to photodecomposition as in the photographic process, the charge carriers are to be captured by the adsorbed reactants, CO₂ and
H$_2$O, for the photochemical surface reaction to commence. The chemical system we utilize must also be able to carry out oxidation and reduction simultaneously just as occurs in the photographic process.

We have been able to produce methane from gaseous CO$_2$ and H$_2$O at the surfaces of an oxide-metal sandwich, SrTiO$_3$-Pt. This was carried on in a 30 torr ambient pressure of the reactants at 300$^\circ$K while illuminating the oxide by band gap (>3 eV) radiation from a filtered mercury lamp. We have utilized a small surface area (~1 cm$^2$) single crystal oxide sample that was cleaned and well-characterized by auger electron spectroscopy (AES) before and after the experiments. The use of well-characterized single crystal surfaces instead of the use of higher surface area powders was deemed necessary because of the possible side reactions due to contaminants, mainly carbon. The formation of CH$_4$ by the nearly thermoneutral reaction

$$2C + 2H_2O \rightarrow CO_2 + \Delta G^\circ = +2.87 \text{ Kcal/mole}$$

has been reported. While large surface area powders or polycrystalline deposits are always carbon contaminated, the small area high purity single crystal sample is readily cleaned by a combination of ion bombardment and chemical treatments before the experiments, thus eliminating the possibility of uncontrolled side reactions. However, as a result of the small surface area of our samples it is more difficult to obtain products in detectable concentrations. The photon assisted reaction is carried out at near atmospheric pressure in a specially constructed isolation cell that is located in the center of an ultra-high vacuum chamber. When the cell is open the sample could be cleaned in situ by ion bombardment or by chemical treatments at low pressures and the surface composition analyzed by AES. Then the cell is closed around the sample, it is pressurized by the introduction of the reactants (CO$_2$ and H$_2$O) and the chemical reaction is carried out at any desired surface temperature while the sample is illuminated through a sapphire window.
There are several advantages in performing photochemical reactions at the solid-vapor interface as compared to the solid-liquid interface. The surface composition and its changes, as a result of the reaction, can be analyzed readily by the modern diagnostic techniques of surface science that require high vacuum. Thus, the reaction mechanism can be studied more easily. The absorption of light and the chemical dissolution of the active surface by the electrolyte are absent and the diffusion of reactants and products to and from the surfaces is more rapid.

There are also important advantages in carrying out photosynthesis by the photochemical reactions of $\text{H}_2\text{O}$ and $\text{CO}_2$ as compared to the photodissociation of water. Although the free energy changes involved in producing some of the small organic molecules, $\text{CH}_4$, $\text{CH}_3\text{OH}$, that may form are larger than for $\text{H}_2$ and $\text{O}_2$ as shown in Table 1, the free energy changes per electron, $\Delta\epsilon^o$, for the reduction of $\text{CO}_2$ to form these molecules are smaller than $\Delta\epsilon^o$ for the electrolysis of water (Table 1). It has been shown that, at least for electrochemical reactions, the ease of sequential reduction or oxidation depends on the relative magnitudes of $\Delta\epsilon^o$ in case of competing reactions. Also, by combined photochemical and catalytic actions of the active surfaces the product distribution in the photosynthetic reaction may be altered.

To verify the elementary steps of the complex photoreaction we have also studied the chemisorption of $\text{CO}_2$ and $\text{H}_2\text{O}$, $\text{CO}$ and $\text{O}_2$ on stoichiometric SrTiO$_3$(111) crystal surfaces in the dark and in light by a combination of techniques of electron loss spectroscopy (ELS) and ultraviolet photoelectron spectroscopy (UPS). These studies will be described at first. Then the photochemical reactions of $\text{CO}_2$ and $\text{H}_2\text{O}$ will be discussed as they were carried out using the SrTiO$_3$-Pt sandwiches, along with the "blank" experiments that were carried out to identify more completely the photochemically active system.
Experimental

a. Equipment and Experimental Procedure

All of the chemisorption experiments were performed in a stainless-steel ultra high vacuum (UHV) chamber evacuated by ion and water-cooled titanium sublimation pumps. The base pressure in the system was in the low 10^{-10} torr range.

A double pass cylindrical mirror analyzer (CMA) with a coaxial electron gun was used as the primary electron source and electron energy analyzer by which electrons emitted into a conical segment with half angle of 42.3° from the axis of the analyzer were collected. In all Auger electron analysis, the CMA was operated at a constant resolution of 1.5 eV. In this way we could resolve detailed structures of the peaks in the $\frac{dN}{dE}$ Auger spectra, and give reliable estimates of strontium to oxygen and oxygen to titanium ratios under different conditions of surface preparation.

A primary electron beam with energies between 60-180 eV was used in the electron energy loss experiments. The electron energy loss spectra (ELS) were obtained either by directly measuring the electron energy distribution $N(E)$ as a function of energy loss or its second derivative $-\frac{d^2N}{dE^2}$. Both methods yielded the same loss peaks except the features in the ELS $-\frac{d^2N}{dE^2}$ spectra were enhanced. The CMA was operated in the retarded mode with pass energy at 50 eV. However, since the primary electron beam was not energy analyzed, the ultimate resolution was limited by the thermal energy spread of the incident electrons which was about 0.5 eV. The energy positions of the loss peaks were independent of incident electron energies in the range of 60-180 eV. All energy loss spectra reported in this paper were obtained with incident energies $\sim$100 eV. The features of these spectra were very surface-sensitive.
In the UPS studies, the cold cathode discharge lamp was operated to generate the HeI spectral line at 21.2 eV. A two-stage differential pumping manifold was employed to minimize the helium leak flow from the discharge lamp into the ultra-high vacuum chamber which maintained a pressure of 1-2×10⁻⁹ torr during all UPS experiments. The mass spectrometer indicated that the pressure rise was due to the increase of helium partial pressure in the chamber. The specimen was positioned with its surface normal coincident with the axis of the CMA. The angle of incidence of the photons on the specimen was 75° from the normal. The analyser was operated with a constant resolution of 0.35 eV. Typically a spectrum could be obtained within 5 minutes.

The specimen used was a 99.99% undoped strontium titanate single crystal with perovskite structure. Samples of (111) orientation, as determined by the Laue back reflection technique, were cut from this crystal and mechanically polished using 0.05 μm Al₂O₃ powders. The specimen was then rinsed in distilled water and mounted on a high density alumina holder, which had a tungsten heater wire located at the back of the sample to allow radiative heating of the crystal. A LEED optics made by Physical Electronics was used to study the surface structure after annealing. Two samples of (111) orientation have been prepared and both gave essentially the same results.

For argon ion bombardment of strontium titanate surfaces, the vacuum chamber was back-filled with argon to a pressure of 6×10⁻⁵ torr. With an accelerating voltage of 2 KeV, the ion bombardment could typically deliver an argon ion beam of 20 μA to the sample surface.

The photoassisted reaction studies were carried out in a specially constructed high pressure - low pressure chamber that is shown in Figure 1. The UHV system is a commercial Varian surface
analysis chamber with low energy electron diffraction, and Auger
electron spectroscopy capabilities. The chamber also has a quadrupole
mass spectrometer for gas analysis and an ion gun for crystal cleaning.
A diffusion pump with cryobaffle were added to the standard ion pump and
titanium sublimation pump to handle the extra gas loads when the isola-
tion cell is opened after an experiment. The system base pressure is
\( \sim 1 \times 10^{-9} \) torr. The isolation cell consists of a cylinder, mounted on a
bellows, which can be raised up over the sample by a screw drive. The
vacuum seal is made with a gold o-ring. With the cell closed gases are
introduced into the cell through connections to an external gas loop.
During an experiment the gases are circulated through the cell and the
loop, which is external to the vacuum system, by a metal bellows pump.
Also in the external loop are: a capacitance manometer (MKS 170M-6B)
and the gas sampling valve for the gas chromatograph that is equipped
with a flame ionization detector (HP 5720A). The sampling volume for
the gas chromatograph is 0.25 ml. The total volume of the cell plus
the external loop is \( \sim 90 \) ml. This isolation cell allows us to run
batch type reactions on well-characterized single crystal surfaces.

The sensitivity of the gas chromatograph flame ionization detector
system using a chromosorb 102 column for the detection of alkanes and
alcohols was excellent, \( \sim 10^{-10} \) moles. Thus, less than monolayer quantities
(\( \sim 10^{15} \) molecules \( 10^{-9} \) moles) could be detected. The detection sensitivity
is much poorer for \( \text{H}_2, \text{O}_2 \) and \( \text{HCOOH} \). The gas mixture could be leaked into
a quadrupole mass spectrometer. However, the high concentration of
gaseous water and \( \text{CO}_2 \) yielded enough fragmentation products with the m/e
ratio of ionized \( \text{O}_2 \) and \( \text{H}_2 \) to eliminate the possibility of their conclusive
detection. As a result our system was very poor at detecting \( \text{H}_2 \), \( \text{O}_2 \) or
\( \text{HCOOH} \) while most sensitive for detecting alkanes and alcohols.

For the photochemical reaction studies the \( \text{SrTiO}_3 \) crystal samples (1cm
diameter and 1mm thick disks) were reduced in a hydrogen furnace at \( 1000^\circ \text{C} \) for
1 hour and then were mounted on a disk of 0.001 inch thick Pt foil and were held
in place by two straps of Pt foil (1mm wide) that were spot welded to the Pt
foil backing (Figure 2). Although the oxide-metal contact was secure it was
only a relatively poor mechanical electrical contact. The oxide-metal sandwich
so prepared was mounted in the UHV chamber. After cleaning by ion bombardment
and annealing by heating in vacuum or in oxygen, an auger spectrum was taken to
determine the surface composition. At this point the isolation cell was closed
and pressurized with the reactant gases. The \( \text{CO}_2 \) was Matheson Research
Grade and was used without further purification. It contained a small
methane impurity which was negligible compared to the methane produced.
The pure water was obtained from Scientific Products and was used after
several cycles of outgassing by freezing with liquid nitrogen while pumping
on the sample. No impurities were detectable in the water by gas chromatography,
or mass spectroscopy.

Band gap radiation was provided by a 500 watt high pressure mercury
lamp in a water cooled housing. Light from the lamp was collimated and
focused on the sample with two quartz lenses. An infrared filter consisting
of a quartz cell filled with \( \text{NiSO}_4 \) solution was placed between the mercury
lamp and the reaction cell, to absorb the heat and transmit the near U.V.
With this arrangement we were able to obtain a photon flux of \( \approx 10^{17} \)
photons/sec on the 1 cm\(^2\) crystal surface.

In order to obtain quantitative determination of the reaction product
concentration, the gas chromatograph was calibrated using pure methane.
Results

A. Selected Properties of SrTiO₃

Stoichiometric SrTiO₃ is an insulator, transparent to visible light (band gap 3 eV). It is cubic (perovskite structure) at 300ºK, but becomes tetragonal at about 110ºK. When the 99.99% undoped strontium titanate obtained from the National Lead Company is reduced by heating in a flow of hydrogen at 1000ºK for two hours it turns black and exhibits a dark conductivity of ~1.0 (ohm-cm)⁻¹. Both stoichiometric and reduced SrTiO₃ were used in our chemisorption and photochemical reaction studies. The AES and UPS Spectra was obtained after ion bombardment at 300ºK to remove the impurities (mostly carbon) followed by annealing at 900ºK. The AES spectra obtained at 300ºK gives peak to peak ratios of $\frac{\text{Sr}(65\text{eV})}{\text{O}(510\text{eV})}$ and $\frac{\text{O}(510\text{eV})}{\text{Ti}(380\text{eV})}$ 1.5 and 2.0 respectively for both the stoichiometric and reduced samples. Thus, the surface composition appears to be similar as judged by AES. It should be noted that the surface composition of SrTiO₃ is temperature dependent as shown in a recent study. The (111) crystal face exhibits a (1x1) LEED pattern when ordered. Ordering, however, requires heating to 900ºK after ion bombardment. While the chemisorption studies were carried out on the ordered (111) surface the chemical reaction studies were carried out mostly on disordered surfaces due to our inability to anneal the oxide surface at high enough temperature on account of poor thermal contacts. The auger peak to peak ratios were not affected by the different degree of ordering of the (111) surface.

The UPS spectra were different for the stoichiometric and reduced (111) surfaces of SrTiO₃ as shown in Figure 3. Both the stoichiometric and
reduced crystals have large concentrations of Ti\(^{3+}\) ions. This is different from the results found for TiO\(_2\), where the stoichiometric sample has no observable Ti\(^{3+}\) concentration.\(^{(7)}\) The transition in the ELS (Figure 4) due to Ti\(^{3+}\) in the reduced SrTiO\(_3\) sample is significantly broadened, indicating the possibility of band formation. There is an additional transition in the UPS (Figure 3) for the reduced sample near \(\sim\)1eV indicating differences in the valence band structure.

**B. Chemisorption of H\(_2\)O, O\(_2\), CO and CO\(_2\) on the SrTiO\(_3\)(111) Crystal Face in Dark and in Light**

When water vapor is introduced into the vacuum chamber at pressures of 10\(^{-6}\) torr, adsorption on the oxide surface takes place. Typical exposures were about 10\(^4\) Langmuir. The UPS N(E) spectra in the region of the Ti\(^{3+}\) transition are shown in Figure 5. The signal due to the presence of Ti\(^{3+}\) ions in the surface decreases upon H\(_2\)O adsorption indicating that much of the Ti\(^{3+}\) is oxidized to Ti\(^{4+}\) by the adsorbed water molecule. The work function is found to increase by 0.4 eV as a result of water adsorption. This may be due to an increase in the band bending near the surface. This is in striking contrast to water adsorption on TiO\(_2\) which causes a decrease in the work function of 0.8eV.\(^{(7)}\)

When water adsorption is followed by illumination of the surface with band gap radiation the Ti\(^{3+}\) signal is only partially regenerated as shown in Figure 5. The work function is not affected.

The UPS difference spectra for water adsorption on SrTiO\(_3\)(111) (1 x 1) and a TiO\(_2\) surface which was reduced by Ar\(^+\) bombardment are shown in Figure 6. The two spectra are quite similar but they are quite different from that
of undissociated water.\(^{(7)}\) Recent calculations by Tsukada et al. indicate that OH\(^-\) may be formed on the reduced TiO\(_2\) surface.\(^{(8)}\) From our results it appears the water adsorbs dissociatively on surfaces of TiO\(_2\) and SrTiO\(_3\) which have significant Ti\(^{3+}\) concentrations. Thus water adsorbs dissociatively on reduced TiO\(_2\) and both stoichiometric and reduced SrTiO\(_3\). In the process of dissociative adsorption of H\(_2\)O the Ti\(^{3+}\) sites are oxidized to Ti\(^{4+}\).

Oxygen chemisorption on the SrTiO\(_3\) (111) crystal face after exposure to \(~5\times10^4\) L increases the work function by \(\Delta\phi = 0.9\) eV. The Ti\(^{3+}\) signal is completely removed by chemisorbed oxygen. This is shown in the UPS N(E) spectra that is displayed in Figure 7. Illumination of the surface with bandgap radiation, after O\(_2\) adsorption, regenerates a significant amount of Ti\(^{3+}\) as shown in Figure 7. However, upon illumination of the O\(_2\) covered surface the work function is reduced by only 0.2 eV which is still 0.7 eV greater than the work function of the clean stoichiometric sample. The fact that the work function does not return to the value of the clean stoichiometric sample upon illumination indicates that not all the adsorbed O\(_2\) is removed by photodesorption.

Both CO and CO\(_2\) give rise to the same UPS difference spectra when adsorbed on the SrTiO\(_3\) surface. The spectrum is shown in Figure 8. The measurements were taken after exposure of the surface to \(~5\times10^4\) L of these gases. The work function is found to increase by 0.3 eV on adsorption of CO\(_2\). The Ti\(^{3+}\) signal is significantly decreased. On illumination there is not noticeable change in either the work function or the Ti\(^{3+}\) signal.

Upon heating the sample after CO adsorption only CO\(_2\) is observed to desorb, indicating that CO may be efficiently converted to CO\(_2\) on the oxide surface.
There is considerable experimental evidence indicating that CO is readily oxidized to CO$_2$ over several transition metal oxide surfaces in addition to SrTiO$_3$. An oxygen ion from the crystal lattice is likely to be used for this purpose. The reduction of CO$_2$ to CO that is commonly observed on many transition metal surfaces does not appear to occur on the oxide surface. Another reaction that converts CO to CO$_2$ is its disproportionation $2$CO$\rightarrow$C+CO$_2$ that may also occur. We cannot rule out this reaction as a possible path to convert CO to CO$_2$, although we do not see the accumulation of much carbon on the oxide surface. During the photosynthetic reaction in the presence of H$_2$O, CO$_2$ and light some carbon does accumulate on the stoichiometric SrTiO$_3$ surface that is detectable by AES. Carbon is never found to accumulate on the reduced SrTiO$_3$ that presents an oxygen deficient surface to the incoming reactants. Since the photochemical activity of the reduced and oxidized surface is nearly identical at 300°K, the reaction that converts CO$_2$ to CO does not appear to be an essential chemical route, in the formation of methane.

In summary, H$_2$O dissociates at least partly on adsorption as indicated by the electron spectra and oxidizes Ti$^{3+}$ to Ti$^{4+}$ in the process. Ti$^{3+}$ is only partly regenerated by bandgap radiation. Oxygen adsorbs in several states on the surface. It desorbs from the state that is associated with the oxidation of Ti$^{3+}$ to Ti$^{4+}$ and the Ti$^{3+}$ sites are regenerated. Other types of chemisorbed oxygen remain on the surface during illumination, as indicated by the work function change. CO and CO$_2$ give rise to the same changes in the electron spectra indicating that they form the same surface species on the oxide surface. It appears that CO is converted to CO$_2$ by a slow surface reaction.
C. Chemisorption of H₂O, O₂, CO and CO₂ on Pt Surfaces

Water is known to chemisorb only poorly on Pt surfaces at low pressures. It remains molecular on the surface and is bound only weakly. Evacuation of the reaction chamber after exposure of the Pt to high pressures (several torr) of water resulted in total removal of the water at room temperature, clearly indicating weak binding. There was no evidence for water dissociation on the Pt surface even at these higher pressures.

Oxygen chemisorbs on Pt single crystal and polycrystalline foil surfaces at low and high pressures. There is evidence for the presence of chemisorbed oxygen as well as the formation of oxide under appropriate experimental conditions. Under conditions of the photochemical reaction studied here, oxygen should mostly be in the chemisorbed state.

Chemisorbed oxygen also interacts strongly with carbon or adsorbed CO on the Pt surface. The kinetics of oxidation of C or CO on Pt have been studied extensively.

CO chemisorbs on Pt with a sticking probability of unity even at very low pressures (∼10⁻⁹ torr). It stays molecular but strongly bound on the metal and it exhibits many binding states with distinguishable heats of adsorption that vary from 32 to 14 kcal/mole. Only surface kink sites will dissociate CO to carbon and oxygen on Pt as indicated by photoelectron spectroscopy studies. Since the concentration of kink sites is a small fraction of the total number of surface sites, most of the CO adsorbed on the Pt surface should remain molecular.

CO₂ adsorbs poorly with a low sticking probability on Pt at low pressures (∼10⁻⁶ torr). At pressures of several torr that are utilized in our photochemical studies, CO₂ adsorbs as indicated by subsequent thermal desorption. Only CO₂ is observed in our thermal desorption
experiments. No carbon buildup on the Pt is observed by AES after exposure to 15 torr CO₂ in the dark. Thus it appears that CO₂ remains largely molecular on the Pt surface in the absence of hydrogen and light and is weakly bound. We find no evidence for the dissociation of CO₂ to CO and O.

D. The Photochemical Reaction of Gaseous H₂O and CO₂ to Produce CH₄ Over SrTiO₃-Pt Sandwiches

The SrTiO₃-Pt sandwich, after cleaning by ion bombardment and heat treatments, is analyzed by AES then enclosed in the isolation cell. The cell is filled with 15 torr H₂O and 15 torr CO₂. The gas composition is analyzed by the gas chromatograph and then the experiment commences. The oxide side of the sandwich is illuminated by light of band gap or larger energy using a 500 watt Hg lamp. A NiSO₄ filter is used to screen out the infrared radiation to avoid heating the sample. The thermocouple that is attached to the sandwich registers less than 10° temperature rise throughout the experiments at 300°K.

Methane gas is produced for the first 10 minutes of the illumination and is readily detected by the chromatograph. The number of methane molecules formed is plotted as a function of time in Figure 9. The initial rate of formation is 2x10¹⁴ molecules/min., which corresponds to a quantum yield of 1 molecule of methane per 10⁴ photons. The total amount of methane formed is ~10¹⁵ molecules, or ~10⁻⁹ moles, that corresponds to about 1 monolayer. The production of methane slows down with time and then stops after 10 minutes. This reaction inhibition is due to a tenacious "poison" since pumping out the reactants and reintroducing fresh H₂O and CO₂ does not regenerate the chemical activity of the surfaces. The photochemical activity is regenerated, however, by renewed ion bombardment and annealing, i.e., complete cleaning of the metal and oxide surfaces. AES indicates the buildup of a monolayer of carbon on the Pt.
There is a thermal generation of methane when a reduced SrTiO$_3$ sample is used in the oxide-metal sandwich. Upon heating to 600°K in the dark, a monolayer of CH$_4$ can be generated just as in light at 300°K. In both cases CH$_4$ production stops after the formation of about a monolayer. It appears that the poisoning reaction is the same in the light-driven and thermally-driven reactions, and we detect a monolayer deposit of carbon on the Pt in both cases. Substitution of CO for CO$_2$ in the reaction mixture does not increase the methane yield. This observation combined with the evidence favoring CO$_2$ in the CO/CO$_2$ equilibrium over oxides seems to rule out CO as an important intermediate in the reaction paths of methane formation.

The following experiments were carried out to prove that CH$_4$ production was indeed the property of the metal-oxide contact. The following experiments all produced no detectable amounts of CH$_4$:

1. The SrTiO$_3$-Pt sample with only CO$_2$ (no H$_2$O) in the presence of light and by heating the sample to 450°K.
2. The SrTiO$_3$ crystal without the Pt foil using CO$_2$ and H$_2$O mixtures and illumination.
3. The Pt foil alone using CO$_2$ and H$_2$O mixtures, both with illumination, and by heating the Pt foil to 450°K.
4. The SrTiO$_3$-Pt sample in a CO$_2$ and H$_2$O mixture using illumination with light of energy less than the band gap of SrTiO$_3$ (light with energy less than the band gap was obtained by placing a Corning glass filter between the NiSO$_4$ solution filter and the reaction cell).

The last experiment indicates that band gap radiation is necessary for the photoassisted production of CH$_4$ from CO$_2$ and H$_2$O. This is consistent with
the observed necessity for band gap radiation to dissociate $\text{H}_2\text{O}$ in the electrochemical cell experiments. These experiments do establish that the photon assisted reaction is a property of the oxide-metal contact system. It appears that the major obstacle in producing more methane may be the deposition of a monolayer of carbon on the Pt surface that seems to block the chemical reaction.
Discussion

There are several important observations that help us to understand the photon assisted process leading to the formation of CH$_4$ from CO$_2$ and H$_2$O:

1. Both the oxide SrTiO$_3$ and the metal are needed to observe the production of methane.

2. The photochemical reaction poisons in 10 minutes at 300$^\circ$K in the reactant mixture. Surface analysis indicates carbon deposition at the Pt surface. The reduced oxide surface remains clean while there is a fractional monolayer of carbon detectable on the stoichiometric SrTiO$_3$. A thermal reaction exists which also produces CH$_4$.

3. Water adsorbs dissociatively on the oxide surface while it remains molecular on the Pt surface. CO is oxidized to CO$_2$ on the oxide surface. O$_2$ chemisorbs on both oxide and metal surfaces. Part of the chemisorbed oxygen that is utilized for the oxidation of Ti$^{3+}$ ions to Ti$^{4+}$ photodesorbs and the Ti$^{3+}$ sites are regenerated.

4. Band gap radiation is necessary to carry out the photochemical reaction.

5. The energy needed to carry out the production of methane from CO$_2$ and H$_2$O is much larger than the band gap of SrTiO$_3$ indicating that the process must occur in a stepwise manner.
The presence of the metal, Pt in our case, appears to be necessary for both catalytic and electrical reasons. Separation of the photon-generated electrons and holes at the oxide surface is likely to be enhanced by the metal-oxide contact. Platinum appears to participate in the \( \text{CO}_2 \) reduction process, most likely through its hydrogenation of the molecule or the reaction intermediates.

While the chemisorption studies indicate that \( \text{H}_2\text{O} \) dissociates on the oxide surface, there is little information at this point on the mechanism of \( \text{CO}_2 \) reduction. Since carbon accumulates at the metal surface it appears that at least part of the carbon cycle involved in the reduction of \( \text{CO}_2 \) to \( \text{CH}_4 \) takes place at the metal surface. One possible reduction scheme would be the conversion of \( \text{CO}_2 \) to CO and then into dissociated oxygen and carbon. The rehydrogenation of C to \( \text{CH}_4 \) that is obtained by the dissociation of CO on Ni, Fe and Rh surfaces appears to be the dominant mechanism for methanation from CO and \( \text{H}_2 \) on these transition metal surfaces. Pt, however, dissociates CO only at kink sites that are present in low surface concentrations, and this process is not likely to account for the formation of the carbon monolayer. Moreover, when CO was substituted for \( \text{CO}_2 \) the photochemical reaction was not enhanced and there is evidence for the oxidation of CO to \( \text{CO}_2 \) at the \( \text{SrTiO}_3 \) surface. Thus we are tempted to rule out this reduction scheme.

A more likely reaction path leading to \( \text{CH}_4 \) formation may be the hydrogenation of \( \text{CO}_2 \) to formic acid (\( \text{HCOOH} \)) or formaldehyde (\( \text{H}_2\text{CO} \)) with further reduction to \( \text{CH}_4 \). Future studies will be directed toward verifying the reaction intermediates -- the carbon cycle leading to \( \text{CH}_4 \) production.

We may suggest a tentative reaction sequence leading to the formation of \( \text{CH}_4 \) from \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) on the oxide-metal sandwich. Water adsorbs dissociatively on the \( \text{SrTiO}_3 \) surface. The photoelectrons and holes
produce H atoms or H\(^+\) ions and O\(_2\) molecules. While O\(_2\) photodesorbs, at least in part [there is evidence from our UPS studies that not all of the chemi-
sorbed oxygen is removed by photodesorption] the H atoms or H\(^+\) ions migrate onto the Pt surface where the hydrogenation of CO\(_2\) and subsequently that of the reaction intermediates occur. It should also be noted that based on the presently available experimental evidence we cannot rule out the possibility of both oxidation and reduction reactions occurring at the oxide surface.

It is notable that CH\(_4\) may be produced in the dark over reduced SrTiO\(_3\)-metal sandwiches. Since the poisoning mechanism seems to be the same as during the photon assisted process, further investigations may permit the steady state production of methane in this circumstance as well. Under certain conditions it can be advantageous to carry out this reaction in the thermal mode instead of under illumination. An added problem of course is the need to stabilize the nonstoichiometric composition in the near surface region. Our UPS studies revealed the likely presence of a Ti\(^{3+}\) impurity band that appears to be the cause of the thermally generated electrons and holes that provide the driving force for this thermodynamically uphill reaction.

There are many future experiments necessary to verify the mechanism of this photosynthetic reaction over the oxide-metal contacts. The role of the metal, electronic or catalytic, should be verified. The effect should be tested using other oxides and other metals as the photochemistry may be markedly changed in this way.

It is likely that other molecules, in addition to methane may also be produced using other appropriate oxide-metal contacts, light of suitable wavelength and gas mixtures of CO\(_2\), H\(_2\)O and N\(_2\). Indeed, light assisted reactions over oxide-metal contacts may provide a new route for the production of many different small molecules.
Since the formation of $\text{CH}_4$ from $\text{CO}_2$ and $\text{H}_2\text{O}$ is obviously a multistep process, semiconductors with smaller band gaps should not be ruled out as photoassista-t agents in these types of reactions.

Acknowledgement

This work was supported by the Division of Basic Energy Sciences of the United States Department of Energy.
References

Figure Captions

Fig. 1 Schematic of ultra high vacuum surface analysis chamber equipped with reaction all.
Fig. 2 Schematic of the SrTiO$_3$(111)-Pt foil sample.
Fig. 3 AES and UPS spectra of stoichiometric and reduced SrTiO$_3$.
Fig. 4 ELS spectra in the region of the Ti$^{3+}$ transition for stoichiometric and reduced SrTiO$_3$.
Fig. 5 UPS N(E) spectra in the region of the Ti$^{3+}$ transition for H$_2$O adsorbed on SrTiO$_3$, before and after illumination.
Fig. 6 UPS difference spectra for H$_2$O adsorbed on TiO$_2$ reduced by Ar$^+$ bombardment and on stoichiometric SrTiO$_3$.
Fig. 7 UPS N(E) spectra in the region of the Ti$^{3+}$ transition for O$_2$ adsorbed on SrTiO$_3$, before and after illumination.
Fig. 8 UPS difference spectra for CO$_2$ and CO adsorbed on stoichiometric SrTiO$_3$.
Fig. 9 Methane production as a function of time of illumination of the SrTiO$_3$-Pt sandwich in the presence of CO$_2$ and H$_2$O.
Table I: The standard free energies, \( \Delta G^\circ \), and the free energy changes per electron, \( \Delta \varepsilon^\circ \), for the reduction of \( \text{CO}_2 \) by water to produce a variety of hydrocarbons.
LEED Optics

Single Crystal Catalyst Sample

To Ion Pump

Sapphire Windows

Bellows Assembly

Sample Manipulator

Auxiliary Electron Gun

Load Bearing Flange

High Pressure Cup

High Pressure Gas Chromatograph

Low Pressure Gas Inlet

XBL762-6489A
SrTiO$_3$(III) surface after Ar ion bombardment at $T=27^\circ$C

SrTiO$_3$(III) surface after Ar ion bombardment at $T=27^\circ$C

SrTiO$_3$(III) surface after reduction in H$_2$ and Ar ion bombardment

SrTiO$_3$(III) surface after reduction in H$_2$ and Ar ion bombardment

Electron Binding Energy (eV)

-16 -12 -8 -4

$E_F=0$

$E_F=0$

XBL 787-5344
ELS for:

(a) Stoichiometric SrTiO$_3$ surface after Ar ion bombardment

(b) Hydrogen-reduced SrTiO$_3$ surface after Ar ion bombardment
UPS Spectra at 27°C for:
(a) Clean SrTiO$_3$ (III)-(1×1) surface
\[ \phi = 4.0 \text{ eV} \]
\[-0.6 \text{ eV} \]

(b) SrTiO$_3$ (III)-(1×1)+5×10$^4$ L H$_2$O surface
\[ \phi = 4.4 \text{ eV} \]
\[ \Delta \phi = +0.4 \text{ eV} \]

(c) After 10$^3$ sec UV Illumination on the SrTiO$_3$ (III)-(1×1)+5×10$^4$ L H$_2$O surface
\[ \phi = 4.4 \text{ eV} \]
\[ \Delta \phi = +0.4 \text{ eV} \]

Electron Binding Energy (eV)

XBL 785-5093
Ar sputtered TiO$_2$(100) + 10$^5$ LH$_2$O

$\Delta N(E)$

$\Delta N(E)$

Electron Binding Energy (eV): $E_F = 0$

$\frac{0}{\text{Ti}} = 1.3$

$\Delta \phi = +0.4$ eV
UPS Spectra at 27°C for:

(a) Clean SrTiO$_3$ (III)-(lxl) surface

(b) SrTiO$_3$ (III)-(lxl) + 5x10$^4$ L O$_2$ surface

(c) After 10$^3$ sec. UV Illumination on the SrTiO$_3$ (III)-(lxl) + 5x10$^4$ L O$_2$ surface

Electron Binding Energy (eV)

XBL783-4757
UPS for SrTiO$_3$(III)-(1x1) + 5 x 10$^4$ CO
\[ \Delta \phi = +0.5 \text{ eV} \]

UPS for SrTiO$_3$ (III)-(1x1) + 5 x 10$^4$ CO$_2$
\[ \Delta \phi = +0.4 \text{ eV} \]
$P_{H_2O} = 17 \text{ torr}$

$P_{CO_2} = 15 \text{ torr}$

Initial Rate $\approx 2 \times 10^{14}$ molecules/minute
<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta G^\circ ) (eV/mole)</th>
<th>( \Delta \varepsilon^\circ ) (eV/electron)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2 + 2 \text{H}_2\text{O} (g) = \text{CH}_4 + 2 \text{O}_2 )</td>
<td>8.30</td>
<td>1.04</td>
</tr>
<tr>
<td>( \text{CO}_2 + 2 \text{H}_2\text{O} (g) = \text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 )</td>
<td>7.15</td>
<td>1.19</td>
</tr>
<tr>
<td>( \text{CO}_2 + \text{H}_2\text{O} (g) = \text{H}_2\text{CO} + \text{O}_2 )</td>
<td>5.32</td>
<td>1.33</td>
</tr>
<tr>
<td>( \text{CO}_2 + \text{H}_2\text{O} (g) = \text{HCOOH} + \frac{1}{2} \text{O}_2 )</td>
<td>2.98</td>
<td>1.49</td>
</tr>
</tbody>
</table>

XBL 785-5064
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.