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PHOTOREDUCTIVE SEQUESTRATION OF CO₂ TO FORM C₁ PRODUCTS AND FUEL

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ABSTRACT

Analytical methods for determining formic and oxalic acids, formaldehyde and methanol have been evaluated and /or optimized for measuring products from photoreduction of CO₂ in illuminated, aqueous suspensions of photocatalysts. An electrophoretic analysis method can detect aqueous formate and oxalate ions at 3 and 1 μM respectively. Recalibration of the Nash formaldehyde determination shows that as little as 0.5 μM can be detected spectrally. Several experiments using suspensions of TiO₂, SrTiO₃ and SrTiO₃ with Cr and Sb were tested in CO₂ saturated solutions. No formate was detected in most experiments. However adding 2-propanol to a CO₂ /TiO₂ suspension gave significant amounts of formate and some formaldehyde by blocking the re-oxidation of formate by semiconductor holes. Loss of C₁ products by re-oxidation is probably an important process limiting the accumulation of formate, formaldehyde and methanol.

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INTRODUCTION

The combustion-based production of CO₂ has evolved into what is perhaps the major environmental challenge of the 21st century. Whereas CO₂ levels in the atmosphere remained stable over the 10,000 years preceding the industrial revolution, that event initiated a steady increase in CO₂ levels over the past 150 years (Stevens, 2000). The resulting 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).

To address global warming, the Department of Energy (DoE) has initiated an extensive program to investigate the technology of capture and storage of CO₂ produced by coal fired plants. Sites now being considered for storing produced CO₂ include the deep ocean, depleted oil and gas reservoirs, deep saline aquifers, and unmineable coal beds (DoE, 2001). Although many of these sites are believed suitable for long-term storage of CO₂, considerable uncertainties surround their permanence and how to monitor such storage sites for loss of CO₂ over centuries.

Another approach is to capture and reduce CO₂ to organic compounds including alkanes that can be reused for fuel. Reduction diverts CO₂ from the atmosphere to C₁ products and fuel and requires no large-scale storage facilities. CO₂ becomes a partly renewable resource that reduces consumption of new fossil fuels and by recycling, the rate of CO₂ production. Reduction of CO₂ is an endoergic process requiring energy input. Sunlight is an abundant though diffuse source of energy capable of effecting the reduction of CO₂ through the use of semiconductor catalysts such as TiO₂, SrTiO₃ or CdS, which form electron/hole pairs on excitation with uv or visible photons (Yoneyama, 1997). If the band gap of the semiconductor exceeds about 2 eV, the conduction-band electrons can reduce CO₂ to a variety of C₁ and C₂ products using hydrogen in water. However, intrinsic photoefficiencies (quantum yields) of photocatalysts currently used for reduction of CO₂ are very low and utilization of the solar spectrum by these catalysts is generally restricted to the uv portion of the spectrum below 400 nm, further reducing overall efficiency.

One objective of this project is to determine if newer photocatalysts reported over the past five-10 years with visible spectral absorbance have improved overall efficiency for reducing CO₂ using solar light. Some of these photocatalysts, are claimed to be active in the visible portion of the solar spectrum for splitting water to hydrogen and oxygen, suggesting they also have surface potentials suitable for reducing CO₂.

Another project objective is to develop process economic estimates for the cost of CO₂ reduction by sunlight in a practical system that uses flue gas as input CO₂. In this effort, we will try to determine spatial requirements (km²) for reduction of fixed amounts of CO₂ using realistic estimates of sunlight intensity and capture efficiency to establish possible conditions and reactor design under which sunlight promoted reduction of CO₂ would be competitive with alternative technologies using current technologies for capture and sequestration of CO₂ from flue gas.

EXECUTIVE SUMMARY

The use of sunlight to reduce CO₂ to C₁ products and to fuel is being investigated as an alternative to sequestration of CO₂ in deep wells or coal beds to effectively make CO₂ a renewable energy source. A number of new photocatalysts have been reported to absorb visible light thereby improving the overall efficiency with which sunlight can be used for effecting chemical reactions and improving the competitive cost for reduction. This project has two main objectives: one is to evaluate some of the newer photocatalysts that absorb in the visible spectrum for their ability to reduce CO₂. The second objective is to develop a qualitative process economic estimate for the cost of reducing CO₂ with sunlight using CO₂ captured from flue gas emitted from a coal-fired plant and using realistic estimates of sunlight intensity, reduction efficiencies and newer designs for utilizing sunlight in a heterogeneous photocatalytic system.

During the reporting period, a new, more sensitive, analytical procedure for formate, acetate, and oxalate ions using capillary ion analysis was optimized and the Nash formaldehyde method was recalibrated to improve sensitivity by a factor of over 100. Photocatalyzed reductions of CO₂ saturated in water were conducted using TiO₂ and SrTiO₃ over periods of 2 to 24 hours using a xenon lamp with irradiance equivalent to mid winter sunlight. However, product formation rates were low; only trace amounts of formaldehyde could be detected and formate formation was significant only when 0.67 mM 2-propanol was added to inhibit re-oxidation of formate to CO₂. One catalyst that absorbs visible light, SrTiO₃ with Cr and Sb, did not appear to exhibit much reactivity in reducing CO₂ although the analysis was complicated by ionic impurities in the catalyst.

EXPERIMENTAL

ANALYTICAL METHODS

CO₂ Analysis

The method for measuring consumed CO₂ was described in the last report (Quarterly Progress Report No. 2, November 2002). Reaction aliquots of 0.1 mL bicarbonate solution were injected into 2 mL stirred 1.0 M H₂SO₄ solution in a sealed glass vessel previously swept with argon (100 mL/min) for 5 min and also housing a CO₂ infrared gas sensor (Vaisala, Model 6MM22, Woburn, MA). Sensor readouts to a voltmeter were calibrated using standard solutions of 0.05 to 0.4 M NaHCO₃. A revised calibration curve for CO₂ now including a zero value is shown in Figure 1. The drop off at 0.05 M CO₂ may reflect the unfavorable partitioning of CO₂ between aqueous and gas phases at low CO₂ concentrations.

Figure 1. Bicarbonate ion calibration using the IR sensor.

Formaldehyde Measurements

The Nash colorimetric method (Nash, 1953) has been used by a number of workers to determine formaldehyde (CH_2O) and formic acid in photoreaction mixtures (Ulman et al., 1982; Sharma et al., 1997). We prepared the calibration curve for formaldehyde from 33% formalin solution diluted to the μM range with Milli Q water. Dilute CH_2O solutions (0.8 mL) were mixed with 0.5 mL Nash reagent (prepared from 150 g ammonium acetate, 3 mL acetic acid, and 2 mL acetylacetone diluted to 1 L with Milli Q water) and allowed to stand for 90 minutes. A series of CH_2O -Nash reagent mixtures with concentrations ranging from 0.033 to 6.67 μM CH_2O were examined by UV/VIS spectrophotometry at 412 nm. The new calibration curve is shown in Figure 2.

Figure 2. Formaldehyde recalibration using the Nash reagent. Absorbances were measured after 90 minutes.

In the Progress Report No.2, we showed calibration curves for formaldehyde concentrations over the range of 33-330 μM CH_2O , which have slopes 100 time smaller than for the recent recalibration curve in Figure 2. The reason for the large discrepancy is not known, but has the effect of extending the sensitivity of the method down to the sub- μM range. A second calibration method, shown in the earlier report and based on the reduction of formate to CH_2O using Mg ribbon and HCl (Ulman et al., 1982; Sharma et al., 1997) was not used.

Methanol Analyses

Methanol analyses were briefly attempted using SPME carbowax DVB fiber probes, designed to concentrate organics in water. The fiber probe is then thermally desorbed in a gas chromatograph/mass spectrometer and, in the case of methanol, the m/e peaks at 31 and 29 monitored. Controls with 33 μM and 330 μM (1 and 10 ppm) methanol gave easy detection for 330 μM methanol in water, with a probable detection limit of 50-60 μM .

Formate Analysis by Capillary Electrophoresis

Capillary ion analysis (CIA) is an alternative analytical method for low concentration anions available in our laboratory, based on electrophoretic separation. When optimized, the method can be used to detect a wide range of anions in the $\sim 1\text{-}3\ \mu\text{M}$ (100 -300 ppb) concentration range. The detection method depends on the displacement by the anion of a proprietary mobile phase, which does absorb in the uv spectrum at 254 nm; hence, the improved sensitivity over HPLC which depends on direct uv absorption by the anion around 210 nm.

Capillary (electrophoretic) ion analyses (CIA) were conducted with a Waters Quanta 4000 Capillary Ion Analyzer (Waters, Franklin, MA) using a 75 μm x 60 cm fused silica capillary column and a pH 5.6, 0.05 molar phthalate buffer with Waters osmotic flow modifier as the electrolyte. Detection is based on indirect uv absorption at 254 nm. Migration times (approximate) of anions in a standard mixture of 10 ppm each of thiocyanate (internal standard), formate, acetate, oxalate, and bicarbonate are 3.1, 3.22, 3.6, 2.85, and 4.2 min, respectively at 25°C.

The instrument was set to acquire data at the rate of 20 bits/s and integrate peak areas in the time corrected mode. Reproducibility of time corrected peak areas for a standard mixture of 10 ppm of thiocyanate (0.17 mM) and 2 ppm (44 μM) formate ions in a series of replicate runs conducted on the same day was good: for thiocyanate the peak area was 429 ± 11 ; formate peak area was 345 ± 11 or about a standard deviation $\pm 3\%$ in both cases. Figure 3 shows a typical CIA plot for thiocyanate and formate.

We judge the detectability by CIA of formate in mixtures to be close to 3 μM (140 ppb or 0.14 $\mu\text{g/mL}$) after correcting for background. Day to day reproducibility of the instrument is only fair with peak areas changing by as much as 20-25%. To account for this variability, all CIA analyses are conducted with standard mixtures of thiocyanate and formate ions.

Figure 3. CIA plot for 10 ppm thiocyanate and 2 ppm formate ions.

MATERIALS AND SUPPLIES

All of the chemicals are reagent grade and used as is. A sample of P-25 anatase TiO_2 was obtained from DeGussa (DeGussa Corp, Cameron ,NJ) and anatase TiO_2 and SrTiO_3 were purchased from Alfa Aesar (Ward Hill, MA) as high surface powders with estimated particle sizes of 30-50 nm; both powders are bright white. SrTiO_3 , doped with Cr and Sb was prepared by sintering a mixture of SrCO_3 , TiO_2 with Cr_2O_3 and Sb_2O_3 at 1100° C for 30 hrs in an alumina boat (Hirano et al., 2000). The resultant powder is tan colored. Hematite-coated TiO_2 was prepared from titanium tetrabutoxide ($\text{Ti}(\text{OBu})_4$) and hematite particles following the procedure of Penpolcharoen et al. (1998). The dry catalyst is an ochre-colored fine powder. CO_2 gas is purified by passing it successively through concentrated sulfuric acid and pure water using gas washing bottles fitted with fritted outlets.

PHOTOCHEMICAL METHODS

Light Source and Photoreactors

The light source for these experiments is a Varian/EIMAC air cooled 300 w xenon lamp. A Pyrex cylinder filled with pure water is positioned directly in the light beam to remove uv light below 300 nm and ir light above 1200 nm.

Light intensity from the xenon lamp was measured using 10 μM ammonium dinitramide solutions (ADN, Yao et al., 1995). ADN has a broad absorption from 260 to 360 nm and photolyzes rapidly in uv light to give products which do not absorb in the near uv. Loss of ADN was monitored in the uv by the loss of absorption at the peak maximum at 284 nm. The half life for ADN was determined to be 140 sec in borosilicate tubes and 110 sec in quartz tubes. For comparison, ADN has a half life in sunlight in late winter of 4 minutes (Mill, 2002). In other words, the xenon source produces about twice the near uv photon flux of winter sunlight under our experimental conditions.

The photoreactors used in these experiments are either 20 mL borosilicate cylindrical tubes (1.5 cm path) fitted with serum stoppers and closures or 100 mL quartz cylindrical tubes (2 cm path) with fitted plastic closures.

Photoreaction Procedures

A typical photoexperiment is conducted by weighing in 0.15% catalyst to 10 to 20 mL CO_2^- saturated pure water or to 0.1 M HCO_3^- solution. If CO_2 is used, the solution and ullage space are saturated with CO_2 for 30-50 minutes before the lamp is turned on. When HCO_3^- solution is used, argon is bubbled through a serum stopped-reactor solution using syringe needles for 30-50 minutes to remove air. A magnetic stirrer is used to ensure that the catalyst remains suspended when the lamp is on. After irradiation, the reaction mixture is passed through a 0.2 μm filter to remove larger catalyst particles and the solution is then ready for product analysis.

BACKGROUND, EXPERIMENTAL RESULTS AND DISCUSSION

The strategy we have used in this project is to start with catalysts, conditions and methods used by other workers which were reported to reduce CO₂ in photocatalyzed reactions to C₁ products such as formate, formaldehyde and methanol. To accomplish this objective, we first developed and tested analytical methods for detecting formate and formaldehyde as well as measuring CO₂ lost from the reaction. These efforts were reported in Quarterly Reports Nos. 1 and 2. Once we could reproduce some of these earlier results with traditional uv photocatalysts such as TiO₂ and SrTiO₃, our plan was and is to examine newer catalysts reported to be active photocatalysts in the visible region of the solar spectrum.

In Table 1, we have summarized reported reduction products from CO₂ using a variety of photocatalysts such as TiO₂, SrTiO₃, CdS, Cu on silicate rock and even the organic dye toluidine blue. Some workers used far uv light, some near or solar uv light and in two cases tungsten lamps were used with visible light- absorbing catalysts. Irradiation times varied from 120 min to 24 hours. Similarly, some experiments used bicarbonate ion, others used flowing or static CO₂.

In most of these previous experiments, formate and formaldehyde are formed although in significantly different concentrations, when corrected for differences in times and volumes. For example, formate yields are reported as 28 μM in 24 hrs (0.5 μmoles/hr) using SrTiO₃ as a photocatalyst with a mercury lamp (uv light) and flowing CO₂ gas (Irvine et al., 1990) and 185 μM in 150 min using TiO₂ with a xenon lamp, bicarbonate ion and oxalate ion as an electron donor (Goren et al., 1990). Sayama et al. (1993) used ZrO₂ and found no formate, only CO. Sharma et al. (1997) used ferrocyanide- modified TiO₂ and claims to have made 2.9 mM formate in 100 min with a tungsten (visible light) bulb. Sharma et al. also showed that at longer times formate slowly disappeared, presumably reflecting both further reduction as well as reoxidation to CO₂. Some workers assert that TiO₂ alone does not reduce CO₂.

Table 1. Reported Products for CO₂ Photoreduction

Catalyst	Products	Concentration	Light Source	Conditions/Time	Citation (Cat. No.)
CdS ZnO SrTiO ₃	HCO ₂ H, H ₂ CO HCO ₂ H H ₂ CO	28 μM, 2.3 μM 24 μM 5 μM	High pressure Hg lamp with Pyrex or quartz	0.15 g/50 mL CO ₂ flow 24 hr	Irvine et al., 1990 (3808)
ZrO ₂	CO	8.6 μM/h	400 W Hg lamp quartz	1 g/350 mL 0.33 M NaHCO ₃	Sayama and Arakawa, 1993 (3809)
SrTiO ₃	HCO ₂ H H ₂ CO MeOH CH ₃ CHO	7.5 μM/h 0.31 μM/h 0.13 μM/h <0.06 μM/h	75 W Hg lamp (high p), 1 g	1 g/160 mL CO ₂ flow at 100 mL/min 60°C	Ulman et al., 1982 (3716)
TiO ₂ /Pd TiO ₂	HCO ₂ H HCO ₂ H	8.3 μM/100 min 1.3 μM/100 min	450 W Xenon >360 nm	3 mL 0.05 M NaHCO ₃ 0.05 M oxalate	Goren et al., 1990 (3729)
TiO ₂ /Fe(CN ₆) ⁴⁻	HCOOH H ₂ CO	29 μM/100 min 0.66 μM/100 min	500 W Tungsten	1 g/150 mL CO ₂ flow 210 min	Sharma et al., 1997 (3754)
Cu/SiO ₂	HCOOH	10 μM	Sunlight, Pyrex	5 g/5 mL CO ₂ (no flow) 10 hr	Ohta et al., 1998 (3750)
Toluidine Blue 1 (-4) M	HCOOH H ₂ CO	220 μM 62 μM	500 W Tungsten	50 mL 1 mM CO ₃ ⁼ no pH effect 120 min	Jain et al., 2001 (3749)
CaFe ₂ O ₄	H ₂ CO CH ₃ OH	38 μM 8.2 μM	High pressure Hg lamp	0.3 g/60 mL 0.01 M NaCH CO ₂ saturated 4 hr	Matsumoto et al., 1993 (3811)

Initial photochemical experiments reported in Quarterly Report No. 2 were conducted using anatase TiO₂ and SrTiO₃ in the presence of HCO₃⁻ ion in an effort to reproduce this earlier work (Miyasaka et al., 1979; Goren et al., 1990; Ulman et al., 1982). We followed both loss of HCO₃⁻ ion from solution and formation of formate and formaldehyde. Although loss of HCO₃⁻ ion indicated significant reduction of CO₂, we were not able to find products using the analytical methods at hand. Part of the problem may have been low detection levels of the HPLC ion exclusion column with uv detection for formate. This is the reason we have switched to the CIA method for detecting formate and other acid anions.

Experiments conducted during the this reporting period focused first, on developing a more sensitive method for detecting formate ion, formaldehyde and methanol, so we could continue photochemical experiments to replicate earlier work and second, on conducting photolysis experiments under conditions where formate has been reported earlier.

Most initial reaction mixtures consisted of 0.1-0.15% by wt of the prewashed semiconductor powder (TiO_2 or SrTiO_3) suspended in 10-20 mL of 0.1 M aqueous HCO_3^- ion or CO_2 -saturated water. If HCO_3^- solution was used, it was acidified with Amberlite resin and degassed on the water pump to remove all of the HCO_3^- ion prior to analysis for acids by CIA. Large amounts of HCO_3^- ion in the reaction mixture made analyses for other anions present in the medium to low μM range impossible. However, impurities in the ion exchange resin interfered with detection of formate in the range of 10 μM . To avoid using resin pretreatment, we switched to CO_2 gas and remove excess CO_2 by brief vacuum treatment. Most experiments in Table 2 use CO_2 -saturated water and excess CO_2 removal has proved to be straightforward. Some CO_2 experiments with added 2-propanol (2-PrOH) as an electron donor to enhance yields of formate and formaldehyde by inhibiting reoxidation of formate to CO_2 with the semiconductor holes (h^+). In one experiment (No.7) use of 0.67 mM (40 ppm) 2-PrOH did lead to formation of a significant amount of formate, whereas a similar experiment (No.4) with 2-PrOH did not give detectable amounts of formate. In general, the experiments to date have not produced significant amounts of formate or formaldehyde above low background concentrations.

Table 2. Experiments on Photoreducing CO_2

Experiment No.	Catalyst (% Loading)	Conditions ^a	Time, h	Results ^b
1	SrTiO_3 (0.10)	0.1 M HCO_3^-	24	HCO_2^- present in control decreased
2	TiO_2 (0.15)	CO_2 flow	24	No HCO_2^- detected No CH_2O detected
3	TiO_2 (0.15)	0.440 mM HCO_2^- under argon	25	320 μM HCO_2^- consumed No CH_2O detected
4	SrTiO_3 (0.15)	CO_2 flow 0.67 mM 2-PrOH	24	550 μM HCO_2^- formed No CH_2O detected
5	SrTiO_3 (0.15)	CO_2 flow 0.75 mM NaOH	24	No CH_3OH detected No HCO_2^- detected No CH_2O detected
6	SrTiO_3 (0.15)	CO_2 static 0.75 mM NaOH	2 4	No HCO_2^- or CH_2O detected No HCO_2^- or CH_2O detected
7	SrTiO_3 (0.1)	CO_2 flow 0.67 mM I-PrOH 0.75 mM NaOH	20	No HCO_2^- detected ~1 μM CH_2O formed
8	SrTiO_3 (SbO_x CrO_y) (0.15)	CO_2 flow	24	No HCO_2^- detected No CH_2O detected

^aIrradiated with 300 w xenon source at 25 cm.

^bDetection limits for HCO_2^- and CH_2O are 3 and 1 μM

To evaluate the re-oxidation of formate by semiconductor holes as an explanation for the low rates of production, we irradiated 0.440 mM formate under argon with 0.15% TiO₂ (No.3). After 20 hrs, 70% of the original formate had disappeared, but because no formaldehyde was detected (above 1 μ M), we conclude that re-oxidation is the most likely explanation for the loss. Sharma et al. (1997) noted that the production of formate declined after 90 minutes irradiation, with a parallel loss of formaldehyde, providing additional evidence that re-oxidation to CO₂ can be an important loss process for C₁ products in the photoreduction.

Reactions (R1) through (R6) indicate that in the absence or near absence of organic material, h^+ will oxidize water to hydroxyl radical (HO or HO $\bullet$) (R3/R4). But as organic compounds form h^+ will begin to oxidize them in competition with oxidation of water (R1/R2). HO will react with itself to eventually form oxygen or directly react with organic compounds to form water and organic radicals as in R5 (Buxton et al., 1988)). The relative importance of competing reactions R1, R3 and R5 is determined by a complicated relation between the rate of formation of HO and the rate of formation of formate through reduction of CO₂.

CONCLUSIONS AND FUTURE WORK

Improved analytical methods have allowed us to measure formation of small amounts of C₁ products under the special conditions where 2-PrOH is added to inhibit re-oxidation of formate to CO₂. Published accounts of CO₂ reduction to formate and formaldehyde describe formation of significantly larger concentrations than we have been able to find in experiments with the same catalysts and under what appear to be similar conditions of light intensity and CO₂ concentrations. We are continuing to evaluate the reaction conditions in our experiments to more

closely replicate results reported earlier. A few experiments in direct sunlight might clarify the situation regarding light intensities in different experiments by different workers.

The common practice in earlier investigations of measuring formate formation by reducing it to formaldehyde and using the Nash method to measure formaldehyde could be one cause of the discrepancy between our results and those of others. If reduction of formate also leads to reduction of dissolved CO_2 , then the yields of formate would be greatly exaggerated.

We plan to investigate in more detail the production of hydrogen formed by reduction of water by the photocatalysts in competition with reduction of CO_2 role played by re-oxidation in limiting the yields of C_1 products in these photocatalytic reductions where oxidation of water by holes is the slow step. Hole oxidation of C_1 products could be competitive with oxidation of water at fairly low concentrations of organics. The implications of re-oxidation for limiting the efficiency of the overall process and the strategies that might be used to mitigate the effects will be explored. Use of sacrificial electron donors such as oxalate or 2-propanol to boost yields of C_1 products does not on the face of it appear to be an economically or environmentally attractive option, but one we will examine.

We plan to initiate a process economic study of photoreduction of CO_2 as applied to a practical solar-driven reduction process using a conservative estimate of the photoefficiency of the reduction coupled with solar intensities as a function of wavelength and CO_2 fluxes scaled to different flue gas sources. Estimates will begin with a very small scale CO_2 source term on the order of 10 kg/day fed into a parabolic solar collector with either suspended or fixed photocatalyst. Whether this type of system can be scaled to the CO_2 fluxes associated with a 500 megawatt coal-fired generating plant remains to be seen.

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