

Photocatalytic reduction of CO₂ to formaldehyde: Role of heterogeneous photocatalytic reactions in origin of life hypothesis

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Received 19 December 2013; received in revised form 26 February 2014; accepted 03 March 2014

ABSTRACT

Photocatalytic reduction of carbon dioxide to formaldehyde was investigated on four semiconductor photocatalysts (FeS, FeS/FeS₂, NiO and TiO₂). The reaction was carried out in continuous flow of CO₂ gas bubbled into the reactor. Semiconductor photocatalysts were characterized by X-Ray diffraction (XRD) and Diffuse Reflectance Spectroscopic (DRS) methods. Sulfide ion was used as hole scavenger. The results show that the TiO₂ has greater photocatalytic activity compared to the other photocatalysts, for example, maximum formaldehyde concentration were 720 and 380 ppm on TiO₂ and NiO, respectively. Addition of carbonate ion causes an increase (around two times) in the concentration of formaldehyde. The yield of the formaldehyde decreased with decreasing concentration of the sulfide ion and the pH of the reaction mixture (from 700 ppm to 500 ppm). This investigation demonstrates that under ultraviolet radiation, carbon dioxide can be reduced to formaldehyde on semiconductor photocatalysts. This reaction could have been a possible chemical route to photosynthesis on the early Earth.

Keywords: Carbon dioxide, Photocatalyst, Reduction, Origin of life.

1. Introduction

Among the numerous questions that scientists ask about nature, those related to the origin of life are probably the most fascinating; and, in this context, questions containing the origin of organic chemicals on early earth are important.

It is commonly assumed that the emergence of terrestrial life depended on the synthesis and stability of organic polymers. The presence of liquid water and small organic molecules on primitive earth are the basic requirements for this phenomenon. It has been generally assumed that two different processes could feed the primitive earth with such organic molecules: (i) exogenous delivery from the solar nebula as meteoritic carbon and (ii) endogenous formation in the atmosphere or oceans. The relative importance of these two processes seems uncertain [1].

After the Millers first experiment on prebiotic synthesis of organics from inorganic feed molecules in the gas mixture (which models atmospheric chemistry on the primitive earth [2]), many scientists try to improve his experiment and modeling techniques.

For example, Miller et al. [3] used other inorganic C sources –instead of methane– for amino acid synthesis.

It was shown that hydrogen to carbon molar ratio plays basic role in amount of products. They also show that the variety of products depends strongly on the carbon source and, in the presence of carbon dioxide and carbon monoxide, only the glycine was obtained. In a computational study, Aylward et al. [4] used a set of chemical reactions to account for the formation of pyridoxal phosphate in the primeval atmosphere composed of cyanoacetylene, diacetylene, carbon monoxide, hydrogen, water, and phosphoric acid. They found that the reactions were feasible from the view point of the overall enthalpy changes. Managadze [5] suggested the universal mechanism for prebiotic synthesis of organic compounds in planetary atmospheres. His experiments showed that in the plasma torch of high velocity impacts -such as the meteoritic impacts during the Late Heavy Bombardment of Earth \approx 4 Ga- various organic compounds could be formed. He also suggested that the configuration of electromagnetic fields in this plasma torch presumably can provide asymmetrical origin of isomers. In an extended review, Balucani [6] addressed the role of elementary reactions in the synthesis of organic molecules in the Universe.

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In this review, a reader can see the use of molecular beam technique coupling with mass spectrometer detection to estimating the reaction rate of the elementary reactions occurred in interstellar medium and planetary atmospheres. Parker et al. [7] used reducing gas mixtures containing H₂S for synthesis of methionine and other organosulfur compounds. They assumed that sulfur containing reducing atmosphere may have existed either in the global primitive atmosphere or in localized volcanic environments on the early Earth.

Another procedure for prebiotic evolution is the synthesis in primordial oceans and pools. Cleaves [8] found that acrolein (an important intermediate in the prebiotic synthesis of several amino acids, pentaerythritol, and various postulated alternative genetic materials) can be synthesized in dilute solution of formaldehyde and acetaldehyde under neutral to basic conditions. Pasek et al. [9] demonstrated that corrosion of meteoritic mineral schreibersite may have significantly contributed to prebiotic synthesis of phosphorylated biomolecules. They found a free-radical reaction pathway for corrosion of schreibersite to form phosphite radicals in aqueous solution. These radicals can form activated polyphosphates and phosphorylate organic compounds such as acetate to yield phosphonates and organophosphates. Ruiz-Bermejo et al. [10] simulated physico-chemical properties of primordial oceans (such as pH, salinity etc.) and showed that carboxylic acids can be synthesized under these conditions. More recently, Saladino et al. [11] proposed that a small organic molecule –formamide– could be the basic molecule for synthesizing nucleic acids.

As an alternative synthetic condition, hydrothermal fluids are very fascinating for scientists. Vitamin B6-type compounds [12], oligopeptides [13] and small organic molecules such as formate and acetate [14] were synthesized under hydrothermal conditions. Simoneit [15] examined physico-chemical conditions necessary for synthesis and stability of organic compounds in hydrothermal fluids on the primitive earth. Bassez et al. [16] analyzed organic components of serpentinized peridotite rocks in the terrestrial upper mantle. In this preliminary analysis, amino acids and long chain n-alkanes were identified.

In industrial chemistry, photocatalytic reduction of CO₂ is one of the interesting ways to synthesis of small important molecules and environmental pollution control [17-21]. But in life origins studies, scientists pay little attention to photocatalytic and photochemical reduction of inorganic carbon. Meierhenrich et al. [22] reported *N*-heterocycles and amines in the room temperature residue obtained after photo- and thermal processing of interstellar ice analogue at 12 K.

Senanayake et al. [23] reported the conversion of formamide to high-molecular-weight compounds attributed to nucleoside bases on the surface of TiO₂ (001) single crystal. This result suggests that oxide semiconductors are active materials for synthesis of high molecular weight organic molecules from smaller molecules. Zhang et al. [24] investigated the capability of ZnS nanoparticles for reduction of aqueous CO₂ under UV irradiation. In the presence of a hole scavenger –sulfide ion– the efficiency was 10% for formate production from CO₂ at pH=6.3. Telegina et al. [25] studied the process of abiogenesis of biologically important compounds such as amino acids, peptides, etc. In their experiment, the photophosphorylation of ADP to ATP on montmorillonite with a yield of 30% was observed. Guzman et al. [26] investigated the reaction of glyoxylate with carbon dioxide on ZnS surface in the presence of ultraviolet (UV) light. Chen et al. [27] irradiated the 1:1:1 mixture of H₂O:NH₃:CO₂ at 16K. These conditions simulate the cometary ices in solar system and star forming regions. Their results indicate that under irradiation with 62-310 nm light, H₂, NH₃, CO, O₂, OCN⁻/OCN⁻, HNCO, CH₄, H₂CO, CH₃OH and HCOOH are synthesized at the ice surface. Delidovich et al. [28] irradiated the formaldehyde aqueous solution with mineral colloids to produce acetaldehyde, glyoxyl, glycolaldehyde and glyceraldehydes. Wang et al. [29] treated newly precipitated ZnS under hydrothermal conditions and found that photocatalytic activity increased markedly with the temperature. Reversible amination of α -oxo acids on the surface of such photo illuminated ZnS was demonstrated.

The early terrestrial atmosphere was composed of H₂O (P \approx 270 bar) and CO₂ (P \approx 40-210 bar) [1]. Under these conditions, the carbon dioxide dissolved in the oceans and the pH of these primordial oceans was between 4.8 and 6.5 [30]. Consequently, in the absence of the oxygen and ozone molecules in the atmosphere, the UV light of the early sun could have initiated photocatalytic reduction of the aqueous CO₂ in the presence of semiconductor colloids. In this work, an aqueous solution of carbonate/carbon dioxide was irradiated in presence of various semiconductor particles (FeS, FeS/FeS₂, NiO and TiO₂) and a hole scavenger (S²⁻). These minerals could be formed in hydrothermal vents in primordial oceans or in volcanic processes.

This study suggests that, in the primitive oceans, freshly synthesized minerals could photocatalytically reduce carbon dioxide to formaldehyde in the presence of the UV light. This molecule can produce more complicated organic molecules such as Carbohydrates etc. that are necessary for life.

2. Materials and Methods

FeCl₂, Ni(NO₃)₂, Ti(OPr)₄, HCl, NaOH and activated carbon were purchased from Merck. Na₂S, CO₂ and N₂ gases were purchased from Across and Roham Gas respectively. All materials were of analytical grade and used without further purification. HPLC grade water (Millipore Q) was used for solution preparation.

2.1. Photocatalyst preparation

FeS synthesis was carried out in a glass vessel. 5 mL Fe²⁺ solution in concentrated HCl (0.2 M iron in 35% HCl solution) was transferred to the reaction vessel and diluted with 20 mL water. Nitrogen was purged into the reaction mixture to avoid the oxidation of this mixture by atmospheric oxygen. Na₂S (100 mL, 0.1 M) was added dropwise to this solution to form the FeS precipitate. Excess amount of sulfide ion was removed as H₂S in the nitrogen flow. The mixture was transferred to a rotary evaporator (for 2 hours) to omit the solvent and remnant H₂S and HCl.

Synthesis of the FeS/FeS₂ mixture was similar to FeS photocatalyst, 25 mL Fe²⁺ solution (0.2 M in concentrated HCl) was transmitted to the reaction vessel and purged with nitrogen. The concentrated solution of sulfide ion (3M, 100 mL) was added rapidly to the iron solution. Mixed precipitate of FeS and FeS₂ were prepared in solution. For removing the water, H₂S and HCl, the mixture was dried in rotary evaporator for 2 hours.

For NiO synthesis, 0.2 M aqueous solution of Ni²⁺ was combined with 25 mL of NaOH solution (0.2M). This hydroxide precipitate was centrifuged and calcined at 500°C for 3 hours.

TiO₂ particles were synthesized using sol gel method. 1 g of titanium tetraisopropoxide was added to methanol and stirred for 30 minutes. After homogenization, 0.5 mL HCl (0.01 M) was added to the solution and stirred for 6 hours until clear solution was obtained. The sol was left for 24 hours to form gel and this gel was calcined at 500°C for 3 hours.

The catalysts were characterized via X-ray diffraction (XRD) and reflectance spectroscopy (DRS) methods.

2.2. Photocatalyst preparation

Photocatalytic experiments were carried out in a 150 mL cylindrical Pyrex reactor. The quartz cap was used

above the reactor for diffusion of UV light and CO₂ purging and avoiding the atmospheric oxygen entering to the reaction mixture. The reaction temperature was maintained in 25±0.1°C with water circulation around the reactor. In a typical photocatalytic run, 50 mL of 1.5 M solution of sulfide ion was mixed with 4.8 g of Na₂CO₃ (1M in reaction mixture) and 0.05 g of photocatalyst (2 gL⁻¹ in reaction mixture) and was irradiated with ultra violet lamp. Reactants were added to the reaction mixture. At appropriate times, 500 μL of aliquots (three different samples in one sampling time) was taken from the reactor and used for chemical analysis.

2.3. Product analysis

Analysis of the reaction products were carried out by an Agilent 7890A series Gas Chromatography-Mass Selective Detector instrument equipped with 60 m HP-5 column. A Wiley library was used for qualitative detection of mass spectra. Concentrations were detected by integration of the peak areas.

A Solid Phase Extraction (SPE) method was used for detection of organic solutes. Appropriate amount of activated carbon was washed with methanol until elimination of any organic material peaks in GC-MS tests and used as adsorbent for SPE analysis. 400 μL of centrifuged sample was added to the 0.01g activated carbon and shaken for 12 hours. The mixture was centrifuged and aqueous supernatant was removed. The solid precipitate was suspended in 300 μL methanol and shaken again. After 1 hour, this mixture was centrifuged and the supernatant solution was injected to the GC-MS instrument.

3. Results and Discussion

3.1. Catalyst characterization

The results of XRD and DRS analysis of colloidal semiconductor catalysts are summarized in Table 1. The crystallite phase of these catalysts was determined from their XRD patterns. The crystallite size was calculated using the scherrer equation, $L=0.94\lambda/b.\cos\theta$ [31]; in which λ is the wavelength of X-ray light, θ is the irradiation angle and b is the relative peak broadening. Table 1 indicates that the crystallite sizes are between 25 and 32 nm.

Table 1. XRD and DRS results for colloidal semiconductors.

Sample Name	Scherrer Crystallite Size (Å)	Band Gap (ev)	Crystallite Phase
FeS	319.6	1.45	Troilite
FeS/FeS ₂	274.9	1.37	Pyrite + Troilite
NiO	249.6	1.36	Bunsenite
TiO ₂	267.9	3.05	Anatase + Rutile

In photocatalytic reactions, the band gap of semiconductor catalysts (energy gap between the valence and conduction band) has a central role. Photocatalytic efficiency, electron-hole recombination rate and product yields depend on the band gap. We estimated the band gap of these catalysts from their diffuse reflectance spectra. The band gaps were calculated from the linear part of the plot of $(\alpha h\nu)^2$ vs. $h\nu$ for each catalyst, α approximately equals $-\ln T$ (T :transmittance). One can see from Table 1 that the band gap of the FeS, FeS/FeS₂ and NiO catalysts are below 1.5 eV i. e. these catalysts are easily activated with ultra violet irradiation. In contrast, Titania has a band gap around 3.2 eV. This band gap was reduced to 3.05 eV when it was synthesized via. sol-gel method.

3.2. Kinetic behavior

Fig. 1 shows the kinetic behavior of the reaction mixture in presence of various photocatalysts at pH 11.2. It is seen from this figure that reduction of carbon dioxide to formaldehyde occurs on all photocatalysts. This figure shows that, the concentration of formaldehyde increases in the presence of photocatalyst under ultra violet irradiation. At the beginning of the reaction, electron-hole pairs are generated under UV irradiation on the photocatalysts. The photo electron then reduces the carbon dioxide to formaldehyde. Sulfide ion act as a hole scavenger and neutralize the holes. The sulfide ion is gradually oxidized to molecular sulfur. After approximately 60 minutes, yellow precipitate of sulfur is observed in the reaction mixture. After the formation of these sulfur particles, the concentration of the formaldehyde decreases due to the consumption of the sacrificial hole scavenger and the resulting photo oxidation of the formaldehyde lead to carbon dioxide. In this figure, the relative photocatalytic activity of NiO is lower than other catalysts because of its photo-corrosion (NiO dissolved in reaction media under UV irradiation during reaction).

Fig. 1 also indicates the relative photocatalytic activity of FeS, FeS/FeS₂, NiO and TiO₂ in photoreduction reaction. As one can see in this figure, in presence of TiO₂, the concentration of the formaldehyde in reaction mixture was higher than other catalysts. FeS, FeS/FeS₂ and NiO had weaker photocatalytic effects, respectively. The higher photocatalytic capacity of the Titania was due to its great photostability in presence of UV irradiation. For other photocatalysts, photocorrosion process dissolves the solid particle in the solution under UV light and thus reduces the photocatalytic capacity of the particles.

As control reactions, two separate photocatalytic reduction were carried out in absence of Ultraviolet radiation and photocatalyst respectively. No

formaldehyde yield was seen in both control reactions. The results are not shown in these Figs.

3.3. Effect of inorganic carbon source

In this study, we used two different types of inorganic C sources; carbon dioxide and carbonate ions (also bicarbonate ion was formed in solution due to equilibrium between various carbon oxides). Carbonate ion does not appear to yield formaldehyde. Figs. 2 to 5 show the production of formaldehyde in the presence of carbon dioxide as C source. One can observe from these Figs. that carbonate ion can promote the production of formaldehyde from carbon dioxide.

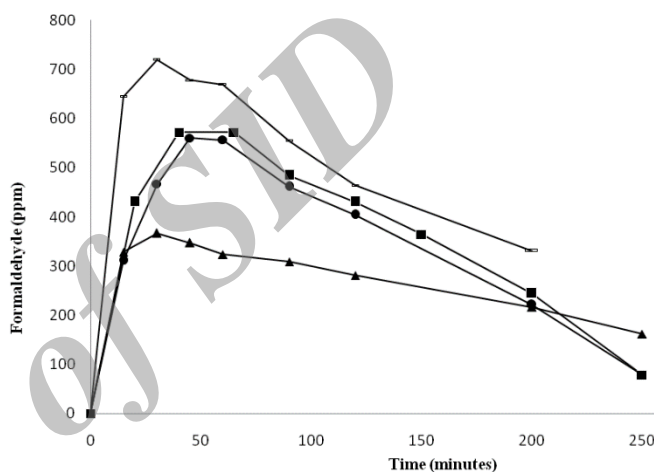


Fig. 1. Concentration of Formaldehyde (ppm) vs. time (minutes) on 2g/L FeS (■), FeS/FeS₂ (●), NiO (▲) and TiO₂ (-) photocatalysts at pH=11.2, 1.5M sulfide and 1M carbonate ions and 60mL/min. flow of CO₂.

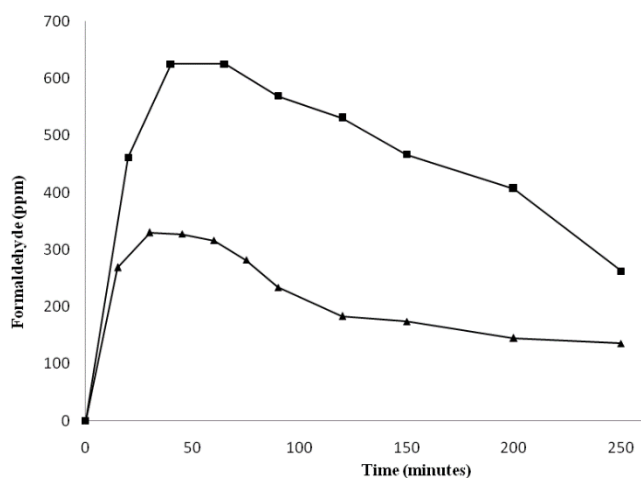


Fig. 2. Concentration of Formaldehyde (ppm) vs. time (minutes) in presence of 60mL/min. CO₂ (▲), and 1M Carbonate ion with 60mL/min. CO₂ (■) as inorganic carbon source on FeS photocatalyst at pH=11.2 and 1.5M sulfide ion.

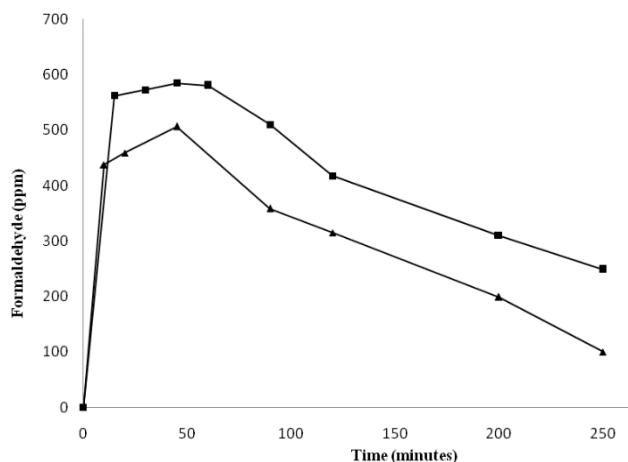


Fig. 3. Concentration of Formaldehyde (ppm) vs. time (minutes) in 60mL/min. CO₂ (▲), and 1M Carbonate ion with 60mL/min. CO₂ (■) as inorganic carbon source on FeS/FeS₂ photocatalyst at pH=11.2 and 1.5M sulfide ion.

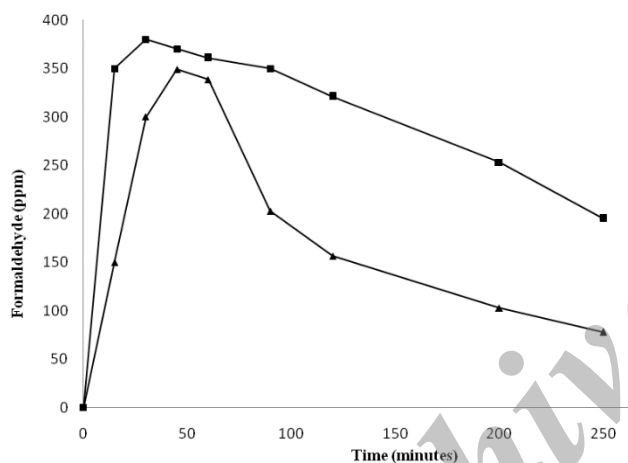


Fig. 4. Concentration of Formaldehyde (ppm) vs. time (minutes) in 60mL/min. CO₂ (▲), and 1M Carbonate ion with 60mL/min. CO₂ (■) as inorganic carbon source on NiO photocatalyst at pH=11.2 and 1.5M sulfide ion.

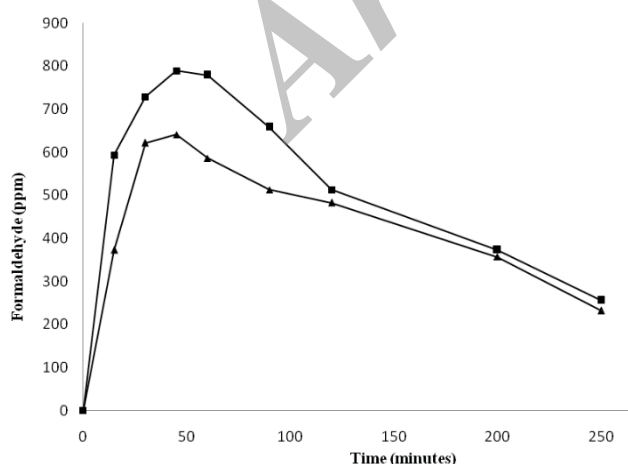


Fig. 5. Concentration of Formaldehyde (ppm) vs. time (minutes) in 60mL/min. CO₂ (▲), and 1M Carbonate ion with 60mL/min. CO₂ (■) as inorganic carbon source on TiO₂ photocatalyst at pH=11.2 and 1.5M sulfide ion.

This observation is due to the reduction of electron-hole recombination rate in presence of carbonate ion as a hole trap. This ion does not react chemically with the photocatalyst and only interact physically with holes on the surface of the photocatalyst [32]. This phenomenon gives suitable time to sulfide ion for electron transfer to the photocatalyst.

3.4. Effect of pH

The aqueous solution of carbon dioxide and carbonate is a buffer. The concentrations of CO_x species in this buffer solution depend on the pH. Any changes in the pH of the solution affect the equilibrium concentration of CO₂. Fig. 6 exhibits the reaction behavior in pH=7.

The yield of formaldehyde was reduced compared to Fig. 1 (pH=11.2). This could be due to the decreased concentration of the carbonate ion (hole trap) at low pH. Also one can see from comparison of Figs. 1 and 6 that decrease in concentration of formaldehyde were greater in case of FeS/FeS₂ photocatalyst. This is due to photo-dissolution of this catalyst at pH=7.

At pH=11.2, CO₂ does not exist in solution in equilibrium condition. In fact, in such mixture, this molecule could only exist in non-equilibrium short lived transition form. In alkaline solution, photoreduction reaction occurs in gas-liquid-solid interface around gas bubbles.

Figs. 1 and 6 show the results of reaction in pH=11.2 and 6 respectively. In pH=11.2, photo-corrosion of NiO catalyst was greater than pH=7; thus the trend was completely different and in Fig. 6 NiO showed better catalytic effects than Fig 1.

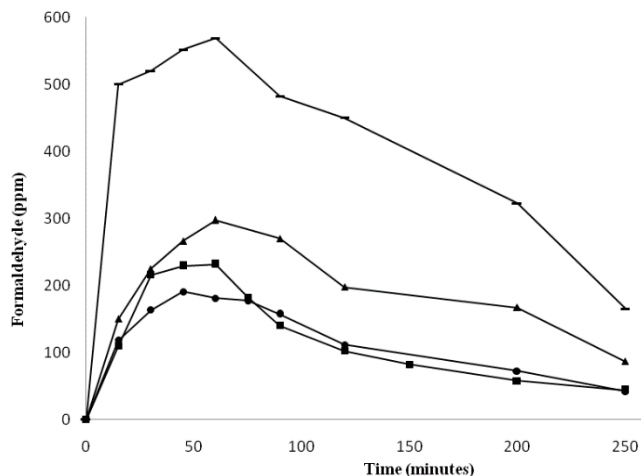


Fig. 6. Concentration of Formaldehyde (ppm) vs. time (minutes) on 2g/L FeS (■), FeS/FeS₂ (●), NiO (▲) and TiO₂ (-) photocatalysts at pH=7, 1.5M sulfide and 1M carbonate ions and 60mL/min. flow of CO₂.

3.5. Effect of carbonate content

As was shown above, carbonate ion could not be reduced in our reaction mixture but can improve the yield of formaldehyde as it serves as a hole trap. Thus we examine the effects of carbonate ion concentration on the reduction of carbon dioxide. Fig. 7 shows the effect of carbonate ion concentration on the formaldehyde yield. One can see from Fig. 7 that carbonate ion concentration decreases the yield of formaldehyde. As mentioned in section 3.3, carbonate ion can interact with the holes in the surface of the photocatalyst and thus inhibit the electron-hole recombination. Reduction in the concentration of this ion causes the increase in electron-hole recombination rate and thus reduces the concentration of the formaldehyde in reaction mixture.

3.6. Effect of sulfur content

In photocatalytic reductions, presence of a hole scavenger is essential. The hole scavenger prevents the recombination of electron and hole on photocatalyst. In this study, sulfide ion act as hole scavenger and the concentration of this ion can affect the reaction kinetics. In Fig. 8, the effect of sulfide ion concentration on formaldehyde production is suggested. Comparison of Figs. 1 and 8 (sulfide concentration 1.5 and 0.3 M respectively) indicates that concentration of product reduced with reduction of sulfide ion concentration. As expected, decreasing of the sacrificial hole scavenger decreases in CO₂ reduction yield.

4. Conclusions

One of the open questions in investigation of the origin of life is the formation of prebiotic molecules on early earth. Existence of semiconductor photocatalyst

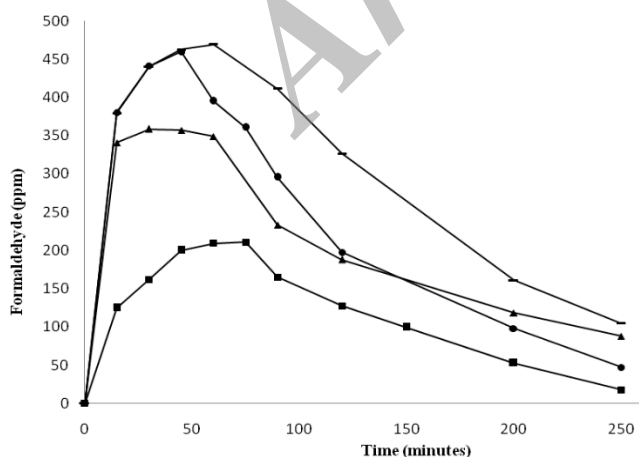


Fig. 7. Concentration of Formaldehyde (ppm) vs. time (minutes) on 2g/L FeS (■), FeS/FeS₂ (●), NiO (▲) and TiO₂ (-) photocatalysts at pH=11.2, 1.5M sulfide and 0.2M carbonate ions and 60mL/min. flow of CO₂.

minerals on early earth such as FeS, FeS₂, ZnS, TiO₂ etc. and possible ultra violet radiation passing through the atmosphere suggests that photocatalytic reduction of carbon dioxide (one of main gasses in early earth's atmosphere) to formaldehyde could act as a possible start point of aggregation of organic materials in the oceans and poles of the early earth.

This study indicates that CO₂ can be reduced to formaldehyde by photocatalytic reaction on such semiconductor colloids. Bubbling of carbon dioxide at the atmospheric pressure into the solution of a hole scavenger ion –sulfide ion– generates formaldehyde in solution. This formaldehyde can react with other chemicals to produce more complicated organic molecules. TiO₂ exhibits higher photocatalytic activity for formaldehyde production compared to other photocatalysts. The yield was increased in presence of carbonate ion. While this ion is not react in our reaction conditions but could interact with the holes and decrease the electron-hole recombination. The highest reaction yield was observed at pH≈11.2 and high concentration of sulfide and carbonate in the aqueous solution.

Acknowledgment

The author is grateful to Ardabil Branch, Islamic Azad University for financial and instrumental supports; and to Mr. Shokri, Mr. Sotoodeh and Mr. Bonabi for their helps in laboratory stage of this research.

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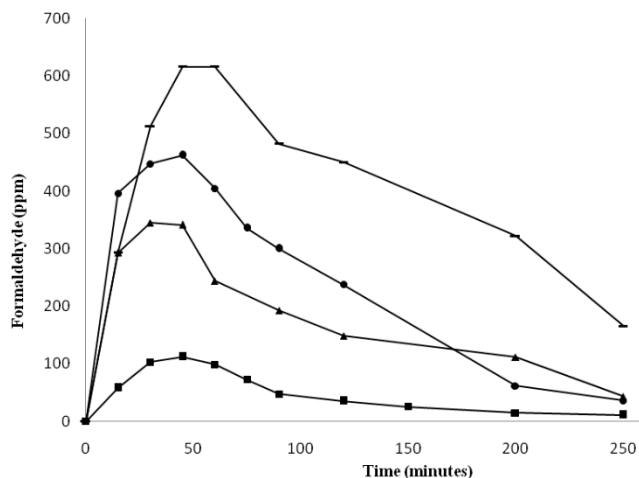


Fig.8. Concentration of Formaldehyde (ppm) vs. time (minutes) on 2g/L FeS (■), FeS/FeS₂ (●), NiO (▲) and TiO₂ (-) photocatalysts at pH=11.2, 0.3M sulfide and 1M carbonate ions and 60mL/min. flow of CO₂.

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