

**INFLUENCE OF REACTION MEDIUM ON CO₂
PHOTOCATALYTIC REDUCTION YIELDS OVER ZnS-MMT**

**VLIV REAKČNÍHO PROSTŘENÍ NA VÝTĚŽKY
FOTOKATALYTICKÉ REDUKCE CO₂ V PŘÍTOMNOSTI ZnS-MMT**

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Abstract

The reduction of CO₂ by photocatalysts is one of the most promising methods since CO₂ can be reduced to useful compounds by irradiating it with UV light at room temperature and ambient pressure. The aim of this work was to assess the effect of a reaction media on CO₂ photocatalytic reduction yields over ZnS nanoparticles deposited on montmorillonite (ZnS-MMT). Four different reaction media, such as NaOH, NaOH+Na₂SO₃ (1:1), NH₄OH, NH₄OH+Na₂SO₃ (1:1), were tested. The pure sodium hydroxide was better than ammonium hydroxide for the yields of the both gas phase (CH₄ and CO) and liquid phase (CH₃OH). The addition of Na₂SO₃ improved methanol yields due to the oxidation prevention of incipient methanol to carbon dioxide. The gas phase yields were decreased by the Na₂SO₃ addition. The best tested reaction medium for the photocatalytic reduction of CO₂ was the solution of sodium hydroxide.

Abstrakt

Redukce CO₂ pomocí fotokatalyzátorů je jedna z nejslibnějších metod, jelikož CO₂ může být redukován na užitečné sloučeniny ozařováním UV zářením při pokojové teplotě a tlaku. Tato práce byla zaměřena na

posouzení vlivu reakčních prostředí na výtěžky fotokatalytické redukce CO_2 v přítomnosti nanočástic ZnS nanosených na montmorillonit (ZnS-MMT). Byla testována čtyři různá reakční prostředí, NaOH, NaOH+ Na_2SO_3 (1:1), NH_4OH , $\text{NH}_4\text{OH}+\text{Na}_2\text{SO}_3$ (1:1). Výtěžky v obou fázích, plynné (CH_4 a CO) i kapalně (CH_3OH), byly vyšší v čistém hydroxidu sodném než v hydroxidu amonném. Přídavek Na_2SO_3 zvýšil výtěžky methanolu a to díky zamezení oxidace vznikajícího methanolu zpět na oxid uhličitý. Výtěžky plynné fáze se však po přídavku Na_2SO_3 snížily. Nejlepším z testovaných reakčních prostředí pro fotokatalytickou redukci CO_2 byl roztok hydroxidu sodného.

Key words: carbon dioxide, photocatalysis, reaction medium, zinc sulphide nanoparticles, montmorillonite.

1 INTRODUCTION

Photocatalysis is described as a change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible or infrared radiation in the presence of a substance — the photocatalyst — that absorbs light and is involved in the chemical transformation of the reaction partners. [1] As photocatalysts semiconductor materials are used because their valence and conduction bands are separated by a band gap. Electrons need to absorb energy for excitation from the valence band to the conduction band. This energy is delivered by absorption of a photon having energy equal to or greater than the band gap energy of semiconductors. Electrons are released from crystalline bonds and excited to the conduction band after absorption of a photon. At the same time, positive holes are generated as well. This whole process is called the generation of electron–hole pairs.

Fujishima and Honda became interested in the heterogeneous photocatalysis when they managed to split water into hydrogen and oxygen in the presence of TiO_2 in 1972 [2]. After this success, research teams all over the world started to investigate heterogeneous photocatalysis. Inoue and co-workers were the first ones who successfully photoreduced CO_2 in the presence of semiconductor powders [3]. The photoreduction of CO_2 has attracted a great interest because the products of this reaction can be used as a fuel and the reduction itself could help to lower the amount of CO_2 in the atmosphere, which would reduce the greenhouse effect. Products gained by the photoreduction of CO_2 differ according to used reaction conditions and photocatalysts. Commercially easy available TiO_2 (Evonik P25) is one of the most commonly used photocatalyst.

The photocatalytic reduction of CO_2 is not effective in pure water because of the low solubility of CO_2 . The solubility of CO_2 is higher in aqueous solutions of hydroxides. In addition, the OH^- ion could act as a strong hole scavenger and forms OH radicals, thereby reducing the recombination of hole–electron pairs. Among the most used reaction medium for the photocatalytic reduction of CO_2 , an aqueous solution of sodium hydroxide [4–11] belongs.

Michalkiewicz et al. compared the efficiency of the photocatalytic reduction in the presence of NaOH and NH_4OH and TiO_2 photocatalysts. Higher yields of methanol were achieved in NH_4OH [12].

Oxygen generated at the photocatalytic reduction of CO_2 can cause the reverse oxidation of incipient methanol. This is the reason why the search for compounds, which will be preferably oxidized by oxygen instead of methanol during the photocatalytic reduction of CO_2 , was carried out. Na_2SO_3 was chosen due to its availability and low price. Liu et al. successfully used Na_2SO_3 for the photocatalytic reduction of CO_2 in the presence of TiO_2 photocatalyst [13].

In this work, we compared the yields of the photoreduction of CO_2 in four different reaction media: NaOH, NaOH+ Na_2SO_3 (1:1), NH_4OH , $\text{NH}_4\text{OH}+\text{Na}_2\text{SO}_3$ (1:1) in the presence of the ZnS-MMT catalyst. The aim of the work was to evaluate which reaction medium gives the best yields of products. The reaction medium NaOH was chosen as comparative as such results were already published [14]. The effect of reaction media on proceeding reactions was discussed.

The yields and selectivity of the CO_2 photocatalytic reduction can be influenced by reaction media. A different reaction medium leads to different products. Products which can be formed during the CO_2 photocatalytic reduction in the presence of the ZnS catalyst are summarized in Tab. 1.

Tab. 1 Products of the photocatalytic reduction of CO₂ in the presence of ZnS

Product	Literature
hydrogen	Fujiwara et al. [15]; Henglein et al. [16]; Inoue et al. [17]; Inoue et al. [18]; Kanemoto et al. [19]; Kanemoto et al. [20]
formic acid	Eggins et al. [21]; Henglein et al. [16]; Inoue et al. [17]; Kanemoto et al. [19]
formate ion	Fujiwara et al. [15]; Inoue et al. [18]; Johne & Kisch [22]; Kanemoto et al. [20]; Kuwabata et al. [23]
carbon monooxide	Inoue et al. [18]; Kanemoto et al. [19]; Kanemoto et al. [20]
acetone	Inoue et al. [17]; Inoue et al. [18]; Kuwabata et al. [23]
methanol	Johne & Kisch [22]; Kuwabata et al. [23]
glyoxylic acid	Eggins et al. [21]
formaldehyde	Chen et al. [24]; Eggins et al. [21]
pinacol	Johne & Kisch [22]
ethanol	Chen et al. [24]
tartaric acid	Eggins et al. [21]
oxalic acid	Eggins et al. [21]

An increase of the yield of products can be accomplished by a change of a reaction medium, for example, Henglein et al. reported higher yields of formic acid in the presence of propan-2-ol than in the presence of methanol [16]. Some other reaction media are shown in Tab 2.

Tab. 2 Examples of reducing agents used for the photocatalytic reduction of CO₂

Reaction media	Literature
tetramethylammonium chloride	Eggins et al. [21]
NaHCO ₃	Inoue et al. [18]
propan-2-ol	Inoue et al. [17]; Inoue et al. [18]; Kuwabata et al. [23]
N,N-dimethylformamide and triethylamine	Fujiwara et al. [15]
water with NaH ₂ PO ₂	Kanemoto et al. [19]; Kanemoto et al. [20]
2,5-dihydrofuran	Johne & Kisch [22]
methanol dehydrogenase with pyrroloquinoline quinone	Kuwabata et al. [23]

The use of some reaction media is debatable because they are being oxidized during the reaction. Products of this oxidization are presented amongst products of the photocatalytic reduction of CO₂ in a reaction mixture. This effect is unfavorable for the potential separation of products.

2 EXPERIMENTAL PART

2.1 Preparation and characterization of the ZnS-MMT photocatalyst

The aqueous solution of Na₂S and cetyltrimethylammonium bromine (CTAB) was added to an aqueous solution of zinc acetate. CTAB prevents ZnS nanoparticles to combine into bigger particles and thanks to this photocatalyst's dimensions stay in the nano area. The whole mixture was vigorously stirred and montmorillonite (MMT) was added. The MMT suspension was shaken during 24 hours. The obtained ZnS-MMT nanocomposite was filtered, washed with deionized water and dried at 60-70°C. The prepared ZnS-MMT nanocomposite was characterized by X-ray powder diffraction, transmission electron microscopy and photoluminescence spectrometry [14].

2.2 Photocatalytic reduction of CO₂

The photocatalytic reduction of carbon dioxide was carried out in a stirred batch annular reactor with the suspended ZnS-MMT catalyst illuminated by the UV 8 W Hg lamp (254 nm). Gas chromatographs equipped with flame ionization (FID) and thermal conductivity (TCD) detectors (GC/FID/TCD) were used for the analysis of gas and liquid reaction products. At first, the solution of a reaction medium with suspended 0.1 g of catalyst was saturated by pure CO₂ (approx. for 30 minutes) until a constant pH value (6.6 – 6.9). Then the photocatalytic reduction of CO₂ was started by switching on the UV lamp. The details of the CO₂ photocatalytic reduction experiment and analytical methods were described in our previous publication [4]. A suitable volume of the liquid phase was set to 100 ml and the catalyst concentration was 1g.l⁻¹ as published recently to fulfill the requirement of the perfect mixing and transmission of UV irradiation in our annular photoreactor [25]. The reaction media, such as 0.2 mol l⁻¹ NaOH, 0.2 mol l⁻¹ NaOH + 0.2 mol l⁻¹ Na₂SO₃ (1:1), 0.2 mol l⁻¹ NH₄OH and 0.2 mol l⁻¹ NH₄OH + 0.2 mol l⁻¹ Na₂SO₃ (1:1), were tested.

Hydrogen carbonate in the liquid phase was determined by the acidimetric titration of reaction mixtures with hydrochloric acid (0.1 mol l⁻¹) using a mixture of Methyl red and Bromocresol green as an indicator. Sulphate was determined by ion chromatography (Dionex, ICS 5000).

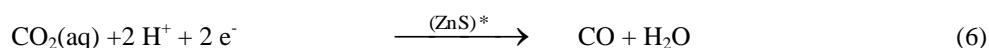
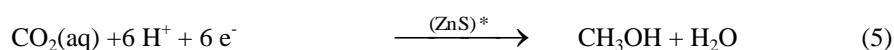
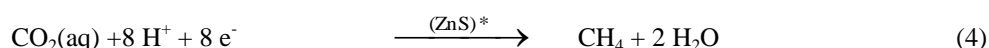
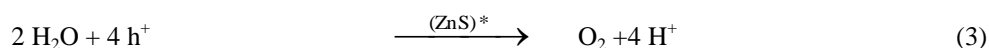
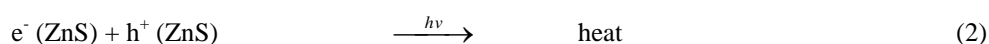
3 RESULTS AND DISCUSSION

3.1 Characterization of ZnS-MMT nanoparticles

ZnS nanoparticles were equally placed on the MMT surface [14]. The particle diameters ranged from 3 nm to 5 nm. Using the Tauc equation, the band-gap energy of 3.89 ± 0.03 eV was calculated from UV spectra of ZnS dispersions. The prepared ZnS-MMT nanocomposite contained about 7 wt% of ZnS and 30 wt% of CTAB. CTAB was also found to be intercalated into the MMT interlayer. Photoluminescence spectra exhibited a strong emission band between 300 nm and 600 nm, which was explained by the vacant ZnS nanostructure.

3.2 Reaction scheme for the photocatalytic reduction of CO₂

A reaction scheme for the photocatalytic reduction of CO₂ by H₂O on ZnS in the presence of Na₂SO₃ is proposed below. Photoexcited electrons (e⁻) and positive holes (h⁺) are produced when incident photons are absorbed in ZnS (Eq. 1, 2). Photoexcited positive holes can be converted by H₂O to H⁺ (Eq. 3). At the same time, CO₂ molecules adsorbed on the surface of ZnS gained electrons and were reduced to CH₄, CH₃OH and CO (Eq. 4-6):



3.3 Effect of reaction medium on the photocatalytic reduction of CO₂

The effect of irradiation time on the formation of CO₂ photocatalytic reduction products was investigated over a period of 0 – 24 h on ZnS-MMT catalysts with different reaction media. Four different reaction media, such as 0.2 mol l⁻¹ NaOH, 0.2 mol l⁻¹ NaOH + 0.2 mol l⁻¹ Na₂SO₃ (1:1), 0.2 mol l⁻¹ NH₄OH and 0.2 mol l⁻¹ NH₄OH + 0.2 mol l⁻¹ Na₂SO₃, were tested.

Fig. 1 shows the evolution of all reaction products as functions of irradiation time for the ZnS-MMT catalyst while sodium hydroxide was used. Two main products were determined: methane in the gas phase and methanol in the liquid phase. Hydrogen and low amounts of carbon monoxide were also detected. The observed order of detected products yields (μmol/g of catalyst) was: H₂ > CH₄ > CH₃OH ≥ CO. Nevertheless, hydrogen isn't a product of the photocatalytic reduction of CO₂ but it is a product of the photocatalytic decomposition of H₂O.

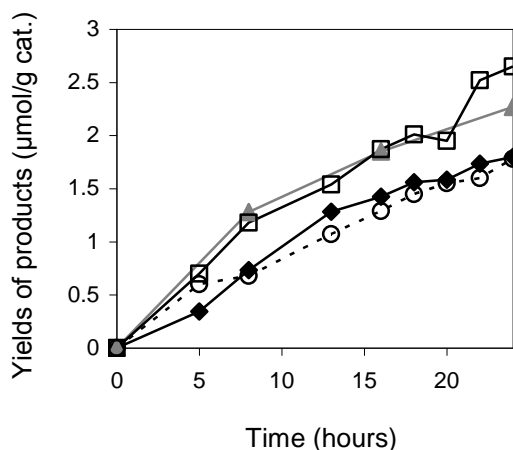


Fig. 1 Yields of all products of the photocatalytic reduction of CO_2 in $0.2 \text{ mol l}^{-1} \text{ NaOH}$ (—◆— $\text{CH}_4/10$; —▲— CH_3OH ; —□— CO ; -○- $\text{H}_2/100$)

Comparisons of the yields in different reaction media are plotted as functions of time (Fig. 2AB, Fig. 3). The yields of products in the gas phase (CH_4 and CO) are shown in Fig. 2A and Fig. 2B. As assumed, the yields of both products increased with illumination time. Sodium hydroxide seems to be a better reaction medium than NH_4OH which is obvious from Fig. 2A.

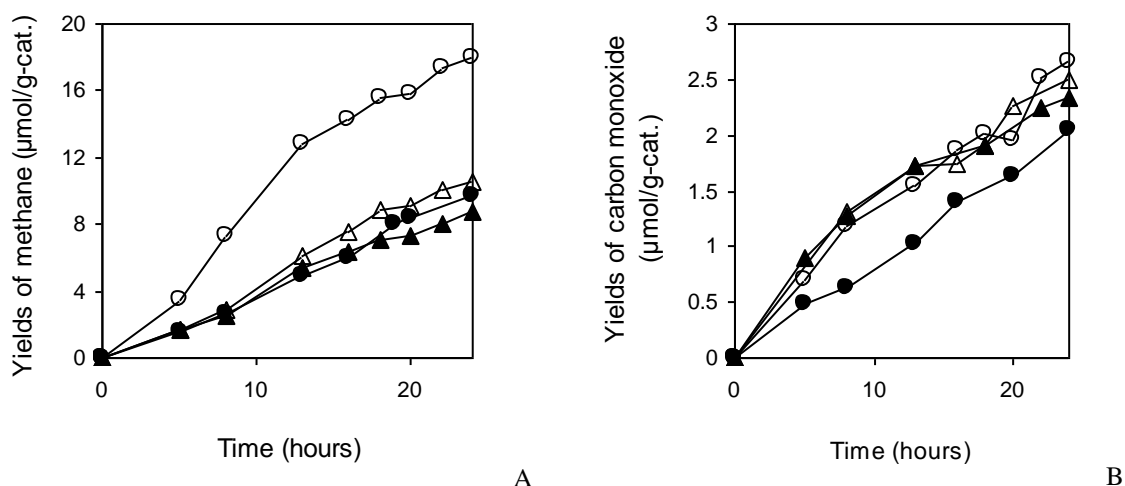


Fig. 2 Dependence of methane (A) and carbon monoxide (B) yields on time in different reaction media (—○— NaOH ; —●— $\text{NaOH} + \text{Na}_2\text{SO}_3$; —△— NH_4OH ; —▲— $\text{NH}_4\text{OH} + \text{Na}_2\text{SO}_3$)

When solutions of NaOH and NH_4OH were saturated by CO_2 , NaOH and NH_4OH were assumed to be neutralized by CO_2 to NaHCO_3 and NH_4HCO_3 , respectively. At $\text{pH} = 6.6$ during the photoreactions, about 60 % of $\text{CO}_2(\text{aq})$ exists in the form of hydrogen carbonate:



These hydrogen carbonates are salts of a strong base and weak acid and a weak base and weak acid, respectively. In aqueous solutions, they hydrolyze forming the equilibrium concentrations of NaOH and NH_4OH as follows:



The concentrations of hydrogen carbonate were determined by the acidimetric titration (Tab. 3).

Tab. 3 Contents of HCO_3^- before and after the photoreduction of CO_2

Reaction mixture	UV	HCO_3^- (g l^{-1})
NaOH + ZnS-MMT	---	11.5
NaOH + ZnS-MMT	24 h	12.4
$\text{NH}_3 \text{ H}_2\text{O}$ + ZnS-MMT	---	12.2
$\text{NH}_3 \text{ H}_2\text{O}$ + ZnS-MMT	24 h	12.5
NaOH + ZnS-MMT + Na_2SO_3	---	8.54

The addition of the hole scavenger Na_2SO_3 to both hydroxides decreased the yields of CH_4 and CO in both cases as obvious from Fig. 2A and 2B.

The yields of methanol as a function of irradiation time are shown in Fig. 3. The yields increased with illumination time again (Fig. 3). Sodium hydroxide gave better yields of methanol than ammonium hydroxide unlike Michalkiewicz [12]. This is more likely caused by the better solubility of CO_2 in NaOH than in NH_4OH .

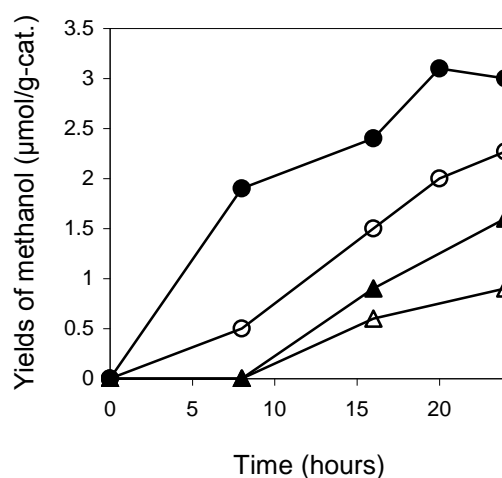
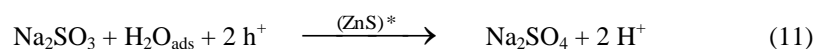


Fig. 3 Dependence of methanol yields on time in different reaction media (○— NaOH; ●— NaOH + Na_2SO_3 ; △— NH_4OH ; ▲— NH_4OH + Na_2SO_3)

The difference between gas and liquid yields consists in the addition of Na_2SO_3 . While the addition of sulphite decreased the yields of products in the gas phase, the yields of methanol in the liquid phase increased. The content of hydrogen carbonate decreased by about 25 % in comparison with the solution without Na_2SO_3 (Tab. 3).

The high concentrations of sulphate determined by ion chromatography were likely formed by the oxidation of Na_2SO_3 . Photoexcited positive holes were converted by Na_2SO_3 to H^+ with the simultaneous formation of SO_4^{2-}



The lower solubility of CO_2 and consequently the decrease of CH_4 and CO concentrations in the gas phase were probably caused by the presence of sulphate. The reverse oxidation of generated methanol back to CO_2 was prevented by the addition of Na_2SO_3 [26].



This effect was probably caused by the primary oxidation of sulphite to sulphate instead of the oxidation of methanol. Oxygen generated from water according Eq.3 was consumed for the oxidation of sulphite as



As confirmed by SO_4^{2-} analysis of reaction solution before and after the CO_2 photocatalytic reduction by ion chromatography.

The data from the longest reaction time span were chosen for the photoactivity comparison. The summations of all products yields in each reaction medium are plotted in Fig. 4. The highest summation was obtained using sodium hydroxide which was also evaluated as the best tested reaction medium.

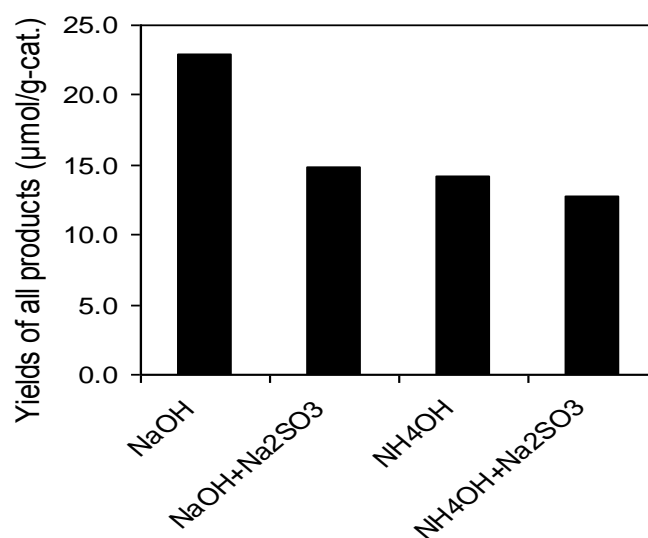


Fig. 4 Summary of all products in each reaction medium after 24 hours irradiation

Since this reactor was used many times before for the photocatalytic reduction of CO₂ and all the results obviously fit the trend of an increment of yields with illumination time we can safely confirm the reproducibility of all published results.

4 CONCLUSIONS

Four different reaction media (the aqueous solutions of NaOH, NH₃ H₂O and their mixtures with Na₂SO₃) were tested for the photocatalytic reduction of carbon dioxide over the ZnS-MMT catalyst. The yields of products were evaluated as a function of time of irradiation.

It was found out that aqueous sodium hydroxide was a better reaction medium than aqueous ammonium hydroxide in the both gas and liquid phases. NaOH is a stronger base than NH₄OH and the solubility of CO₂ is higher in NaOH. It probably caused higher yields of the photocatalytic reduction of CO₂. After addition of Na₂SO₃ a decrement of methane and carbon monoxide in the gas phase and an increment of methanol in the liquid phase were observed. This effect was likely caused by the primary oxidation of sulphite to sulphate, which blocked up the oxidation of generated methanol back to carbon dioxide. The addition of Na₂SO₃ would be especially used if the reaction will be arranged without the gas phase.

The main product of the photocatalytic reduction of CO₂ was methane; the highest yields of methane were obtained in aqueous sodium hydroxide. For that reason the aqueous 0.2 mol l⁻¹ NaOH solution was evaluated as the best tested reaction medium.

ACKNOWLEDGEMENTS

The financial support of the Grant Agency of the Czech Republic (P107/11/1918), the Czech Ministry of Education, Youth and Sports, research project MSM 6198910019 and EU project CZ.1.05/2.1.00/03.0069 is gratefully acknowledged.

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RESUMÉ

Redukce CO₂ pomocí fotokatalyzátorů je jedna z nejslibnějších metod, jelikož CO₂ může být redukován na užitečné sloučeniny ozařováním UV zářením při pokojové teplotě a tlaku. Tato práce byla zaměřena na posouzení vlivu redukčních prostředí na výtěžky fotokatalytické redukce CO₂ v přítomnosti nanočástic ZnS nanosených na montmorillonit (ZnS-MMT). Byly testovány čtyři různá redukční prostředí, NaOH, NaOH+Na₂SO₃ (1:1), NH₄OH, NH₄OH+Na₂SO₃ (1:1). Výtěžky v obou fázích, plynné (CH₄ a CO) i kapalně (CH₃OH), byly vyšší v čistém hydroxidu sodném než v hydroxidu amonném. Přídavek Na₂SO₃ zvýšil výtěžky methanolu a to díky zamezení oxidace vznikajícího methanolu zpět na oxid uhličitý. Výtěžky plynné fáze se však po přídavku Na₂SO₃ snížily. Nejlepším z testovaných redukčních prostředí pro fotokatalytickou redukcí CO₂ byl roztok hydroxidu sodného.