

# Photo-catalytic reduction of carbon dioxide to methane using TiO<sub>2</sub> as suspension in water

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## Abstract

Photo-catalytic reduction of CO<sub>2</sub> to methane was studied in CO<sub>2</sub>-saturated aqueous solution in presence of TiO<sub>2</sub> photo-catalyst (0.1%, w/v) as a suspension using 350 nm light. CO<sub>2</sub> methanation rate was very much enhanced in the presence of 2-propanol as a hole scavenger. In addition to CO<sub>2</sub> reduction, photo-catalytic reduction of methanol in N<sub>2</sub>-purged system was also tried but no methane was generated in presence of TiO<sub>2</sub> without 2-propanol. The yield of methane was quite low even in presence of 2-propanol in this system. In the methanol photolysis CO<sub>2</sub> was found to be the main product with a yield of 60 × 10<sup>-8</sup> mol to 200 × 10<sup>-8</sup> mol. This shows that the generation of CH<sub>4</sub> from CO<sub>2</sub> does not proceed via methanol as an intermediate under these conditions. In the aerated system also, methane was produced during photolysis of TiO<sub>2</sub> suspension in presence of 2-propanol and its yield was comparable to that in CO<sub>2</sub>-saturated system. This suggests that surface-adsorbed as well as in situ generated CO<sub>2</sub> are equally responsible for methane formation through photo-reduction in presence of TiO<sub>2</sub>. In the aerated system, 45 μmol CO<sub>2</sub> was produced by photo-degradation of 2-propanol. In O<sub>2</sub>-saturated system, the methane yield was lower as compared to that in aerated system whereas CO<sub>2</sub> yield was higher. Overall, the yield of methane was quite high if extrapolated to per gram of TiO<sub>2</sub>.

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**Keywords:** CO<sub>2</sub>-reduction; Methane; TiO<sub>2</sub>; Methanol; Hole scavenger

## 1. Introduction

Use of solar energy in solving environmental problems has become very important [1–7]. Insecticides, herbicides and pesticides used in farming with subsequent run-off to catchments areas lead to organic contamination of soil and water. Other common examples of pollution are accidental leakages and spills and continuous discharge of waste by-products in effluent streams from essential industries. This water eventually contaminates ground and surface water, which is the primary source of human contact with toxic chemicals. In order to tackle this problem, extensive researches are being carried out to develop advanced physicochemical methodologies for the elimination of hazardous chemicals from air, soil and water. Purification procedures based on photochemical reactions are potentially useful for this purpose. Photochemical means to destroy organic pollutants through oxidation as well as to convert them to useful material by means of reduction are the best ways to tackle this problem.

The use of sunlight to convert potentially harmful organic chemicals to harmless mineral products or useful organic chemicals at accelerated rates by the use of a comparatively cheap and non-toxic photo-catalyst is an attractive alternative and is aimed at restoration of the environment. Various photo-catalysts such as TiO<sub>2</sub>, ZnO, WO<sub>3</sub>, CdS, ZnS, SnO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub> have been tried independently or in the mixed or metal-doped forms for this purpose [4,5]. The initial step in TiO<sub>2</sub> photo-catalysed oxidation is believed to be the formation of both hydroxyl radicals and super oxide radical anions [2]:



In presence of air,



Thus two species, OH ( $E^\circ = 2.72$  V) [8] a strong oxidant and O<sub>2</sub><sup>-</sup> ( $E^\circ = -0.33$  V) [9] a weak reductant, are generated from the above photo-catalysed oxidation. In the absence of oxygen, OH radical, a strong oxidant, and e<sup>-</sup>, a

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strong reductant, are the reactive species generated on photolysis of TiO<sub>2</sub> in aqueous medium [10–12]. In the presence of an OH or an h<sup>+</sup> scavenger, it is possible to use TiO<sub>2</sub> for photo-reduction processes.

Conversion of CO<sub>2</sub> into methane or other organic substances is of importance not only for the development of alternative fuel sources, but also for the prevention of rise in temperature due to green house effect. Photo-catalytic reduction of CO<sub>2</sub> using photosensitive semiconductor powders has been studied in aqueous solutions [13], liquid CO<sub>2</sub> [14] and high pressure CO<sub>2</sub> [15]. Electrochemical reduction of CO<sub>2</sub> has also been extensively studied using various kinds of metals as cathode, producing CO or formic acid as the main product depending on the kind of cathode materials [16,17] and the route for the electrochemical reduction reaction has been established. Kaneco et al. [15] have reported that CO<sub>2</sub> reduction does not take place in the absence of electron donors. They tried 2-propanol as a hole scavenger during photo-catalytic reduction of high pressure CO<sub>2</sub> using TiO<sub>2</sub> suspensions in water and reported the formation of methane. In the work on photo-reduction of liquid CO<sub>2</sub>, no gaseous products were observed; only formic acid was reported as a reduction product [14]. Methanol, formaldehyde and traces of formic acid in liquid phase and CO in the gas phase were reported as the products for photo-catalysed reduction of CO<sub>2</sub> in the TiO<sub>2</sub> suspension containing copper powder [18]. Low yield of methane was observed after a long illumination time when KHCO<sub>3</sub> was used in the system.

We have studied the photo-reduction of CO<sub>2</sub>, and methanol in the presence of TiO<sub>2</sub> semiconductor in aqueous medium at room temperature under normal pressure conditions and observed the formation of methane in presence of 2-propanol. The main objective of this work is to elucidate the mechanism of CO<sub>2</sub> methanation in the presence of 2-propanol as a hole scavenger at ambient conditions and also to compare the results with deoxygenated and oxygenated systems where methane was also produced.

The results show methane can be produced under these experimental conditions with good yield.

## 2. Experimental

TiO<sub>2</sub> (anatase, –325 mesh) was purchased from Aldrich and used as received. A quartz cell of 16.5 ml capacity having a gas purging inlet and a gas sampling port was used for photo-irradiation with 350 nm light using Rayonet photoreactor having photon flux  $4 \times 10^{15}$  photons cm<sup>-2</sup> s<sup>-1</sup>. The amount of solution used for photolysis experiments was 5 ml. The ambient gas after photolysis of sample was analysed by gas chromatography (GC) using a poropak Q-S column of 2 m length and diameter 1/8 in. Helium was used as a carrier gas. Five hundred microlitres of gaseous sample was injected into the GC for the analysis of CH<sub>4</sub> and CO<sub>2</sub>. Thermal conductivity detector (TCD) and flame ionization detector (FID) were used for analyzing the gaseous samples. Gases such as CO<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub> used in the experiments were of the best quality available from Indian oxygen. The purged/saturated systems were photo-irradiated at normal atmospheric pressure and at room temperature. The estimated values of methane yield have an error of  $\pm 10\%$ .

## 3. Results

The yield of methane obtained from the photolysis of different solutions containing various concentrations of 2-propanol in the presence of 0.1% (w/v) TiO<sub>2</sub> is given in Table 1. The amount of solution used for photolysis experiments was 5 ml and it contained 5 mg of TiO<sub>2</sub>. In the CO<sub>2</sub>-saturated system, the yield of methane observed after 5 h photolysis was  $5.4 \times 10^{-8}$  mol and was found to increase with the time of photolysis as shown in Fig. 1. It may be mentioned here that this yield of methane was

Table 1

The yield of methane obtained from photolysis of 5 ml solutions containing 0.1% TiO<sub>2</sub> (w/v) in the presence and absence of 2-propanol

Systems	Photolysis time (h)	Yield of CH <sub>4</sub> and CO <sub>2</sub> ( $\times 10^8$ mol <sup>-1</sup> ) from a solution containing 2-propanol					
		0 M		0.05 M		0.5 M	
		CH <sub>4</sub>	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>
CO <sub>2</sub> -saturated	0	0	–	0	–	0	–
	5	2.2	–	2.1	–	5.4	–
	10	12.2	–	11.7	–	29.7	–
N <sub>2</sub> -saturated	0	0	0	0	0	0	0
	5	0	0	0	0	2.2	20
	10	0	0	2.3	20	11.3	50
Aerated	0	0	0	0	0	0	0
	5	0	0	12.4	2930	22.1	3150
	10	0	0	11.3	4350	31.5	4650
O <sub>2</sub> -saturated	0	0	0	0	0	0	0
	5	0	0	10.2	3740	11.3	4000
	10	0	0	13.2	6500	15.3	5870

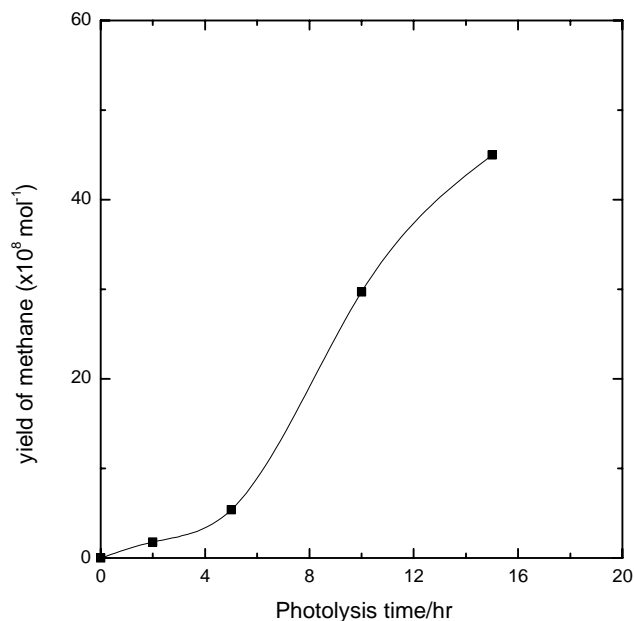


Fig. 1. Plot of yield of methane vs. photolysis time obtained for  $\text{CO}_2$ -saturated 2-propanol solutions containing 0.1%  $\text{TiO}_2$ .

obtained by using 5 mg of  $\text{TiO}_2$  in 5 ml of solution and extrapolated methane per gram of  $\text{TiO}_2$  will be 200 times this value. In the  $\text{N}_2$ -purged system, methane yield was quite low even after 10 h of photolysis whereas in the aerated system the yield of methane was higher as compared to that in  $\text{N}_2$ -purged solution and is comparable to that in  $\text{CO}_2$ -saturated system. Methane yield was also found to increase with increase in concentration of 2-propanol in the presence of the photo-catalyst under identical conditions. It can be seen that the yield of methane more than doubled when 2-propanol concentration was increased from 0.05 to 0.5 M. No methane was obtained on photolysis of a  $\text{CO}_2$ -saturated solution containing 0.5 M 2-propanol in the absence of  $\text{TiO}_2$  photo-catalyst. Hence, methane formation is not due to any thermal decomposition or photolytic degradation of 2-propanol. It is mainly due to the photo-catalytic reduction of carbon dioxide over  $\text{TiO}_2$ . 2-Propanol acts as a positive hole scavenger [15,19] and reacts with the positive hole ion (an oxidizing species) producing a reducing radical  $[(\text{CH}_3)_2\text{C}^\bullet\text{OH}]$ . The hole ( $\text{h}^+$ ) and OH radical have similar properties. The rate of reaction of 2-propanol with the hydroxyl radical has been reported [20] to be  $1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  in aqueous system. The low yield of methane found in  $\text{N}_2$ -purged system has been explained earlier [13,21,22] as due to the reduction of dissolved  $\text{CO}_2$  which is present in water even in a deaerated system.  $\text{CO}_2$  produced from degradation of 2-propanol can also contribute to this photo-reduction.

To evaluate the optimum concentration of  $\text{TiO}_2$  for photo-reduction of  $\text{CO}_2$ , photolysis experiments were carried out in  $\text{CO}_2$ -saturated systems containing 0.5 M 2-propanol in aqueous solution and varying the concentra-

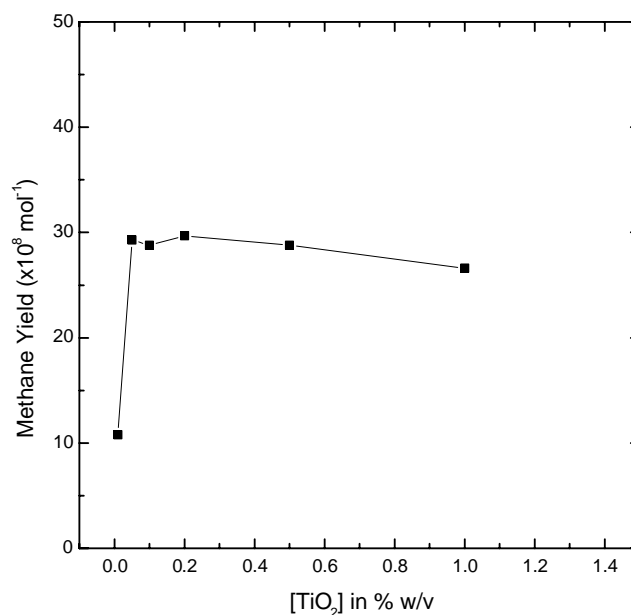


Fig. 2. The yield of methane obtained from various concentrations of  $\text{TiO}_2$  in  $\text{CO}_2$ -saturated system containing 0.5 M 2-propanol after 10 h photolysis.

tion of  $\text{TiO}_2$  as suspension. The results obtained are shown in Fig. 2. It was found that at  $\geq 0.05\%$   $\text{TiO}_2$  concentration, the methane yield reached an optimum value. Earlier, most of the researchers have used 0.5% or higher concentration of the semiconductor [13,21,22]. Using a high concentration of  $\text{TiO}_2$  makes the solution more opaque and the fraction of light absorbed by the system may actually decrease with increasing concentration of  $\text{TiO}_2$  leading to a lower yield of  $\text{CH}_4$ . In our experiment we have used only 0.1%  $\text{TiO}_2$  (w/v) and it has given much higher values of  $\text{CH}_4$  yield from  $\text{CO}_2$  as compared to those reported earlier [15]. The yield of methane without the hole scavenger [15,19] has not been measured earlier but under this condition a measurable amount of methane was found.

Methanol, formic acid and formaldehyde are well known products formed during  $\text{CO}_2$  reduction process [13,21–25]. Methanol is an intermediate for methane formation from  $\text{CO}_2$  as per the mechanism ( $\text{CO}_2\text{--HCOO}^-/\text{HCOOH--CH}_3\text{OH--CH}_4$ ) as reported elsewhere [18,23]. If it is so under the present system, it should be possible to produce methane by two-electron reduction of methanol also. Hence, we tried to reduce methanol by the photo-catalytic reduction route in the presence of  $\text{TiO}_2$ . The results obtained are listed in Table 2. As seen from this table, no methane was produced in the absence of 2-propanol. Even in the presence of 2-propanol the yield was low and almost constant for different concentrations of methanol. It is known that 2-propanol is a better hole scavenger than methanol [15]. This may be the possible reason why no methane was produced in the presence of methanol alone. These results probably indicate that methanol may not be an intermediate

Table 2

The yield of methane with respect to photolysis time from N<sub>2</sub>-purged system containing various concentrations of methanol and 2-propanol in presence of 0.1% TiO<sub>2</sub>

Systems containing		Photolysis time (h)	Photolysis yield ( $\times 10^8 \text{ mol}^{-1}$ )	
Methanol (M)	2-Propanol (M)		[CH <sub>4</sub> ]	[CO <sub>2</sub> ]
0	0	0	0	0
0.5	0	10	0	63.2
0.005	0.5	10	7.7	76.5
0.05	0.5	10	6.3	135.0
0.5	0.5	10	7.7	202.5

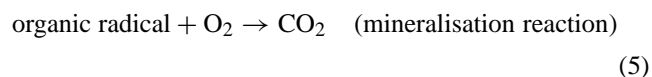
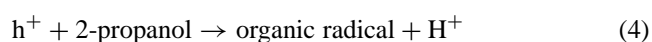
in the reduction of CO<sub>2</sub> under this condition. Whatever yield of methane was obtained in this system may be coming from the photo-reduction of dissolved CO<sub>2</sub> or CO<sub>2</sub> produced during photolysis of methanol and 2-propanol.

#### 4. Discussion

It is clear from Table 1 and Fig. 2 that the amount of semiconductor catalyst and the ambient are very important for the reduction of CO<sub>2</sub>. If we compare the yield of methane in CO<sub>2</sub>, N<sub>2</sub> and aerated systems we find that a higher yield of methane was obtained in both aerated and CO<sub>2</sub>-saturated systems whereas in N<sub>2</sub>-purged system the yield was lower. On photo-irradiation, hole (h<sup>+</sup>) and e<sup>-</sup> are generated as explained in reaction (1). The presence of 0.5 M 2-propanol is enough to scavenge h<sup>+</sup> an oxidizing species, to produce a reducing species (reaction 4). In N<sub>2</sub>-purged system, absence of oxygen does not allow 2-propanol to mineralize to CO<sub>2</sub> to a great extent as indicated by the small amount of CO<sub>2</sub> produced. The low yield of methane generated in this system may be due to the photo-reduction of a small amount of CO<sub>2</sub> produced by photolysis of 2-propanol. It is worth noting that without 2-propanol as a hole scavenger methane was not produced in the N<sub>2</sub>-purged system. This agrees well with the views reported earlier [15,19] about the requirement of a hole scavenger.

The time profile obtained for the yield of methane as shown in Fig. 1 indicates that the methane yield in CO<sub>2</sub>-saturated system increases with the photolysis time after a small induction period. With increasing light exposure time, more and more photo-electrons are generated resulting in increased reduction yield. The high yield of methane in the aerated system was unexpected. However, this can be explained as due to greater mineralization of 2-propanol to CO<sub>2</sub> by photo-oxidation in the presence of O<sub>2</sub>. The mineralization of the alcohols has also been discussed earlier [26,27] and the process enhances with the modification of photo-catalysts. Thus, CO<sub>2</sub> generated in situ, on the surface of the semiconductor has an important role in the formation of methane under this condition. This is also supported by the results obtained in the case of an oxygenated system where the concentration of oxygen is expected to be five times higher and the methane yield was lower. The yield of

methane depends on both the concentrations of oxygen and the hole scavenger (2-propanol). This can be explained in better way by the following proposed mechanism:



In the O<sub>2</sub>-saturated system, where oxygen concentration ( $1.2 \times 10^{-3} \text{ mol dm}^{-3}$ ) is five times higher as compared to that in the aerated system, part of e<sup>-</sup> react with O<sub>2</sub> rather than CO<sub>2</sub>, thus reducing the yield of CH<sub>4</sub>. In the aerated system although CO<sub>2</sub> yield is lower than that in O<sub>2</sub>-saturated system, more e<sup>-</sup> are available for photo-reduction of CO<sub>2</sub>. Further, if it can be assumed that the surface adsorption of CO<sub>2</sub> is higher than that of O<sub>2</sub>, then the surface-adsorbed CO<sub>2</sub> has better chance of getting reduced to methane. In this system, it is difficult to differentiate surface-adsorbed CO<sub>2</sub> from the in situ generated CO<sub>2</sub>, possibly at the surface of the photo-catalyst.

Acetone [15], formed due to oxidation of 2-propanol was observed in our experiments also. We also tried to estimate propane as a photolysis product of 2-propanol under these experimental conditions but its yield was very low both in aerated and O<sub>2</sub>-saturated systems. Thus, methane may not be formed directly on photolysis of 2-propanol, but may be a product of photo-reduction of CO<sub>2</sub> produced from 2-propanol. Photolysis of 2-propanol system without TiO<sub>2</sub> semiconductor did not yield any methane.

The yields of methane given in Tables 1 and 2 and Figs. 1 and 2 were obtained from 5 ml samples containing 0.005 g of TiO<sub>2</sub> as suspension. These values can also be extrapolated to yield per gram of TiO<sub>2</sub> per hour as in other reports available in the literature. For example  $29.7 \times 10^{-8} \text{ mol}$  of methane obtained in the CO<sub>2</sub>-saturated system after 10 h photolysis (see Table 1) is equivalent to  $6 \mu\text{mol h}^{-1} \text{ g}^{-1}$  after extrapolation. Hence, the yield of methane per gram of TiO<sub>2</sub> per hour of photolysis is quite high in comparison to that reported even for high pressure CO<sub>2</sub> system [15]. This may be due to the fact that when one employs 0.5% or more

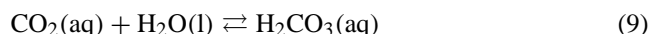
TiO<sub>2</sub> (w/v), less light is absorbed by the system due to the opacity leading to low methane yield as observed earlier [15].

Polychromic light sources, such as Xe arc lamps, medium pressure mercury lamps and blacklight bulbs were used in most of the photolysis experiments in the presence of the semiconductor catalyst. In such systems quantum efficiency or photonic efficiency cannot be calculated because of scattering/reflection of the incident light by TiO<sub>2</sub> semiconductor particles [28]. Hence, in our studies we do not report the quantum yield of the reduction products.

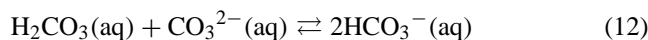
CO<sub>2</sub> has a solubility of about 90 cm<sup>3</sup> per 100 ml of water. In aqueous solution, it exists in many forms [29,30]. First, it simply dissolves,



Then, equilibrium is established between the dissolved CO<sub>2</sub> and H<sub>2</sub>CO<sub>3</sub>, carbonic acid



Only about 1% of the dissolved CO<sub>2</sub> exists as H<sub>2</sub>CO<sub>3</sub> a weak acid, which dissociates in two steps,



Our experimental results especially in the aerated system indicate that the methanation of CO<sub>2</sub> is occurring on the surface of semiconductor catalyst but not through methanol pathway. Also, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, though present in the CO<sub>2</sub>-saturated system, do not take part in the formation of methane under the experimental conditions as shown by experiments conducted with these systems. The above results agree with the mechanism reported [15] for the methanation process for high pressure CO<sub>2</sub> where the authors explained the methane formation through C• radical generation mechanism and also with the mechanism suggested by Anpo et al. [31] where the authors used different types of active titanium oxide to reduce CO<sub>2</sub> with H<sub>2</sub>O by photo-irradiation.

## 5. Conclusions

Photo-catalytic reduction of CO<sub>2</sub> using TiO<sub>2</sub> suspension in aqueous solutions containing 2-propanol as a hole scavenger leads to the formation of methane. CO<sub>2</sub> reduction is not possible without light or without a positive hole scavenger such as 2-propanol. CO<sub>2</sub> reduction on TiO<sub>2</sub> was found to be very less in the absence of a hole scavenger. Methane was also produced on photolysis of aerated 2-propanol solutions containing TiO<sub>2</sub>. The methane formed in this system could be explained as due to the production of CO<sub>2</sub> (produced from 2-propanol mineralization) on the surface of the

semiconductor. In the oxygen-saturated system, the yield of methane was lower due to competition for e<sup>-</sup> by both O<sub>2</sub> and CO<sub>2</sub>.

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