

# Photocatalytic transformation of CO<sub>2</sub> to CH<sub>4</sub> and CO on acidic surface of TiO<sub>2</sub> anatase



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## ABSTRACT

Recently, many studies have demonstrated that carbon dioxide can be converted to methane on TiO<sub>2</sub> surface by a photocatalytic process. We show that such a photo-reduction can be significantly affected by the presence of an acidic proton in powder samples of titania. Using in situ absorption gas-phase rovibrational spectroscopic detection of CH<sub>4</sub>, CO and CO<sub>2</sub>, we demonstrate that proton enhancement positively affects transformation of intermediate derivatives to methane during the photo-irradiation process via several reactions in which the electron transfer inside titania is coupled to oxygen transfer to the Ti<sup>3+</sup> centers of TiO<sub>2</sub> structure. The yield of CH<sub>4</sub> or CO depends on the surface conditioning of titania: the formation of CH<sub>4</sub> is boosted by a presence of adsorbed HCl, while the formation of CO is boosted by adsorbed H<sub>2</sub>SO<sub>4</sub>.

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## 1. Introduction

Due to the increasing greenhouse gases concentration in the atmosphere, global warming effect represents a substantial problem for our planet. Carbon dioxide, a product of excessive combustion of fossil fuels, belongs to the most significant atmospheric contributors. Beside other possible processes of CO<sub>2</sub> removal, a chemical conversion of carbon dioxide into energy containing fuel offers cheap and feasible solution. Hence, photocatalytic technologies toward carbon dioxide conversion into fuel have attracted the attention of many researchers and swiftly became promising in many applications. A critical review of CO<sub>2</sub> photoconversion [1] covers the current progress of photocatalytic reactions of CO<sub>2</sub> over the metal oxides. It is known that photo-irradiated metal oxides can reduce (with a small quantum yield) carbon dioxide with water adsorbed on the oxide surface to form highly energetic molecules such as methane, methanol, acetone, formaldehyde, formic acid, acetone and others depending on the specific conditions [2,3].

Recently published studies [4,5] related to application of Indoped TiO<sub>2</sub> and montmorillonite modified TiO<sub>2</sub> nanocomposites indicate considerable improvement of CO<sub>2</sub> reduction and the enhancement of the photocatalytic process. The photochemical reaction pathway from CO<sub>2</sub> to methane involves several reaction steps producing both stable and unstable molecular intermediates.

The detailed description of the methanogenesis on titania [6,7] indicates the existence of charge-transfer reactions involving two

or more electrons from the titanium dioxide [7,8] or a different mechanism of one-electron reduction from the bulk solvent, which includes trapped electron Ti<sup>3+</sup> centers on the titania surface.

Formation of surface oxygen defects (V<sub>O</sub>) on the anatase surface is a topic that has been investigated several times over the past decade [9–14]. It has been shown [10] that there is lesser tendency toward formation of V<sub>O</sub> defects on the anatase (101) than on the (110) surface of rutile. This finding has been ascribed to the lower stability of adjacent 4-fold Ti<sup>3+</sup> sites on the anatase (101) surface than of adjacent 5-fold-coordinated Ti<sup>3+</sup> sites on the rutile (110) surface. Density functional theory (DFT) [12] calculations indicate that the forming of an oxygen surface defect requires about 0.5 eV higher energy than forming of a bulk vacancy.

To explain the importance of Ti<sup>3+</sup> centers and their role in heteroatomic photocatalytic reactions on the surface of metal oxides, several studies have been carried out. Zapol et al. showed two fundamental reactions on Ti<sup>3+</sup> centers [6,15]:



Ti<sup>3+</sup> surface centers occur with reactant and intermediate molecules serve as electron acceptors (A) that are adsorbed on these centers.



In addition to reaction (1) there is another class of electron-transfer reactions on oxide surfaces. These reactions occur only in certain types of molecular adsorbates, denoted as the RB adsorbates, where R is an organic group and B is a base that involves a heteroatom (such as O or N), for which the Ti<sup>3+</sup> center becomes an acceptor, forming a bond to the heteroatom. The proposed reac-

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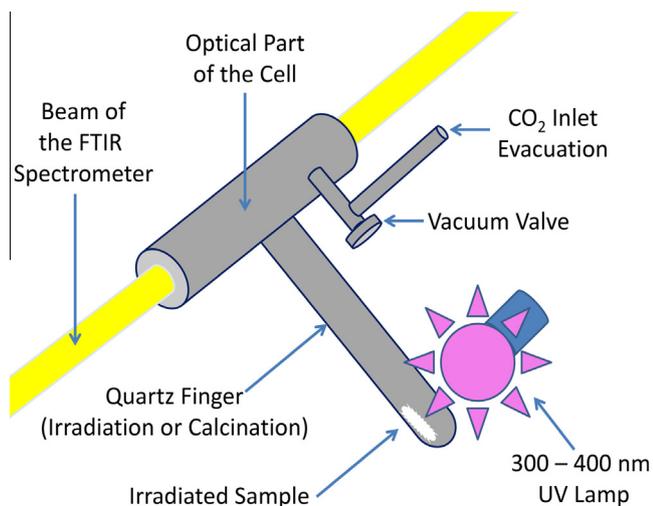
tion mechanism (2) has broad implications for various processes from photocatalytic energy conversion to methanogenesis and diagenesis in planetary chemistry on Mars, Saturn's moon Titan or Urey-like reduction mixtures on early Earth.

## 2. Materials and methods

In our photochemical experiments, three UV broadband light sources (each of them 300–400 nm,  $\lambda(\text{max}) = 366$  nm, 160 W, E27 Omnilux Lamp) in an air flow cooled photo reactor vessel have been used to irradiate powder  $\text{TiO}_2$  in presence of 10 Torr of  $\text{CO}_2$ . Three types of  $\text{TiO}_2$  samples have been prepared as follows:

- (1) 1 g of neat crystalline  $\text{TiO}_2$  anatase prepared in a closed all-glass vacuum apparatus from titanium tetrachloride (99.98% Aldrich) vapor hydrolyzed with deionized water ice. The synthesis is described in details in our previous works [16–21]. The sample is referred to as A100, indicating annealing temperature of 100 °C after the synthesis. According to our previous results, such sample contains 17% wt of adsorbed HCl.
- (2) 1 g of pure crystalline  $\text{TiO}_2$  anatase A100 was additionally calcinated at the temperature of 450 °C in vacuum. This sample is further referred to as A450. According to our previous results, the calcination temperature of 450 °C removes all traces of HCl and water. This A450 titania sample has been subsequently treated with 1 ml of 10%  $\text{H}_2\text{SO}_4$ .
- (3) Comparative measurement has been performed with pristine A450 (free from  $\text{H}_2\text{SO}_4$ ).

The irradiation and subsequent detection of products using FTIR spectrometry [22,19,23–25] have been conducted in situ in a 20 cm long (2.5 cm diameter) glass optical cell with  $\text{CaF}_2$  windows equipped with a 25 cm long quartz tube finger where irradiation of the  $\text{TiO}_2$  took place (see Fig. 1). Samples were frozen at –5 °C and contacted with 10 Torr of  $\text{CO}_2$ . The quartz finger was placed into the irradiation vessel for 70 h. Spectral measurements have been performed in selected time intervals using a Bruker IFS 125 HR spectrometer ( $\text{CaF}_2$  beam splitter, InSb detector) [26–29] in a spectral range from 2000 to 5000  $\text{cm}^{-1}$ . 50 spectral scans have been accumulated with a resolution of 0.02  $\text{cm}^{-1}$  using the Blackmann–Harris apodization function.



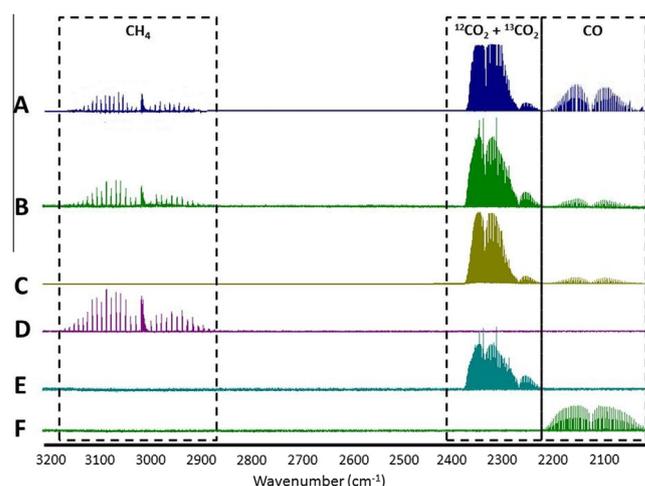
**Fig. 1.** Scheme of the optical cell equipped with a quartz finger for calcination and irradiation.

## 3. Results and discussion

Using FTIR spectra, methane and carbon monoxide have been identified as the main products in our irradiation experiments. Their formation was observed in both experiments with UV irradiation of  $\text{CO}_2$  in presence of A100 (A100 contains adsorbed HCl) and A450 sample (free from HCl) but treated with 10%  $\text{H}_2\text{SO}_4$ . Fig. 2 shows the most significant spectral bands in our experiments. The upper three panels show  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{CO}$  bands in our experimental samples, while the lower three panels show standard pure gas spectra of  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{CO}$  measured on the same apparatus. Detailed spectra of methane  $\nu_3$  band measured after 37 and 70 h of A100 irradiation are shown in Fig. 3. A comparative measurement was also performed with A450 in absence of any acid. In this case, methane concentration remained under detection limit. However, we detected 0.05 Torr of carbon monoxide.

Time evolution of gas phase concentrations is depicted in Fig. 4. At the end of the irradiation, the concentration of  $\text{CH}_4$  in the gas phase above A100 anatase sample is significantly larger than that of  $\text{CO}$ . On the other hand, A450 sample with  $\text{H}_2\text{SO}_4$  produces more  $\text{CO}$  than  $\text{CH}_4$  (the methane band is about 4 times weaker than that of  $\text{CO}$  and is therefore difficult to distinguish it in the picture). Treatment of  $\text{CO}_2$  in presence of A100 anatase (panel A) resulted in formation of 0.33 Torr of methane, while A450 (panel B) treated with  $\text{H}_2\text{SO}_4$  provided 0.26 Torr of  $\text{CH}_4$ . In the case of A100 sample, the ratio of carbon monoxide to methane was significantly lower than in case of experiment with A450 treated with  $\text{H}_2\text{SO}_4$ .

The mechanism of  $\text{CH}_4$  and  $\text{CO}$  formation has been discussed in details by Zapol et al. [6] A short scheme is shown in Fig. 5.  $\text{CO}_2$  is adsorbed on the  $\text{TiO}_2$  surface and accepts electron excited from the valence band to conduction band by UV radiation. Reaction with acidic proton leads to the formation of formyl HC–O radicals which subsequently transform to glyoxal OCH–HCO. In the following reaction steps, glyoxal again accepts protons and electrons and reacts with a donor of hydrogen (HCO,  $\text{CH}_3\text{OH}$  etc.) [30–32] forming acetaldehyde. During these reaction steps, water is released. In the final step which involves photolysis, acetaldehyde splits to  $\text{CO}$  molecule and methane. According to our results, this radical mechanism involving only  $\text{CO}_2$  as a parent molecule in  $\text{CO}$  and  $\text{CH}_4$  synthesis is very likely.



**Fig. 2.** The main absorption bands of  $\text{CO}_2$  ( $\nu_3$ ),  $\text{CH}_4$  ( $\nu_3$ ) and  $\text{CO}$  after 70 h of irradiation. Panel A shows an experiment with A450 +  $\text{H}_2\text{SO}_4$ , panel B A100, panel C experiment with pristine A450, panel D depicts standard spectrum of  $\text{CH}_4$ , panel E standard spectrum of  $\text{CO}_2$  and panel F standard spectrum of  $\text{CO}$ . All spectra have been scaled to fit the picture, so quantitative data cannot be deduced from this picture.

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