

# Artificial Photosynthesis: Methane production from CO<sub>2</sub> by photocatalytic route

Luis De la Torre S, María Teresa Chaparro, M. Manuel Román A  
A. Aguilar Elguézabal.\*

<sup>1</sup>*Catalysis Laboratory, Centro de Investigación en Materiales Avanzados, S.C.*

*Miguel de Cervantes 120 Complejo Ind. Chihuahua, Chihuahua, Chih. 31110 México.*

\* alfredo.aguilar@cimav.edu.mx.

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## Abstract.

Titanium dioxide has been widely studied as photocatalyst for the decomposition of organic compounds. Recently, many efforts have been focused on the research of the capability of TiO<sub>2</sub> to work in the opposite way, i.e., on the photocatalytic synthesis of organic compounds from inorganic molecules (CO<sub>2</sub> and H<sub>2</sub>O)<sup>1-3</sup>. In this work we report the effect of several elements that have been considered on technical literature as potential promoters for the synthesis of methane from CO<sub>2</sub> and H<sub>2</sub>O, using commercial TiO<sub>2</sub> as photocatalyst. Results shown that some of the elements really improve the performance of TiO<sub>2</sub> for the synthesis of methane, however reaction rate is low and there are challenges to face from the reactor design point of view that must be faced to develop an industrial process.

## Experimental part

Photocatalysts were prepared from Degussa P25 TiO<sub>2</sub>, which was modified by incipient wetness impregnation, using aqueous solutions of precursors. After impregnation photocatalysts were dried at 110 °C. To evaluate the activity to produce methane, a cylindrical reactor was used, which has quartz windows of 3.5 cm of diameter and a volume of 30 mL. For each photocatalytic test, 0.5 g of photocatalyst were spread on the bottom of reactor. For reaction, CO<sub>2</sub> (99.99%) was bubbled through a saturator filled with water, CO<sub>2</sub> flow was of 20 mL/min, and then saturated gas was injected to reactor to replace air in reactor chamber. The continuous flow of CO<sub>2</sub>/H<sub>2</sub>O was maintained during two hours, thereafter, valves were closed and exposition to radiation started by means of a Hg lamp. Exposition to radiation was maintained for 14 h, thus methane concentration here reported was obtained for this reaction time for all samples. Methane formation was determined by gas chromatography.

**Table 1.** Elements used to modify commercial TiO<sub>2</sub>.

Precursor	Element content (% wt)
Samarium acetate (Sm(OOCCH <sub>3</sub> ) <sub>3</sub> •3H <sub>2</sub> O)	0.1, 0.05
Cupric chloride (CuCl <sub>2</sub> •2H <sub>2</sub> O)	0.025; 0.05; 0.1; 0.125; 0.2
Calcium chloride (CaCl <sub>2</sub> )	0.14
Chloroplatinic acid (H <sub>2</sub> (PtCl <sub>6</sub> ) •2H <sub>2</sub> O)	0.1
Vanadium pentoxide (V <sub>2</sub> O <sub>5</sub> )	0.1

## Results

The higher activity for copper was obtained at 0.05% wt, lower and higher content of Cu does not improved results. For the others elements, samarium presented best results. Vanadium was selected due to its well known capability to promote oxidation/reduction reactions, nevertheless improvement was very low. Platinum which is highly active on hydrogenation/dehydrogenation reaction has no effect on methane formation. In the case of calcium, this element was used to give stability to TiO<sub>2</sub> as an aid to avoid the irreversible reduction of TiO<sub>2</sub> surface during methane formation, since part of surface of photocatalyst change color from white to slight purple, indicating the partial reduction of photocatalyst; however improvement was lower than the obtained for samarium and copper.

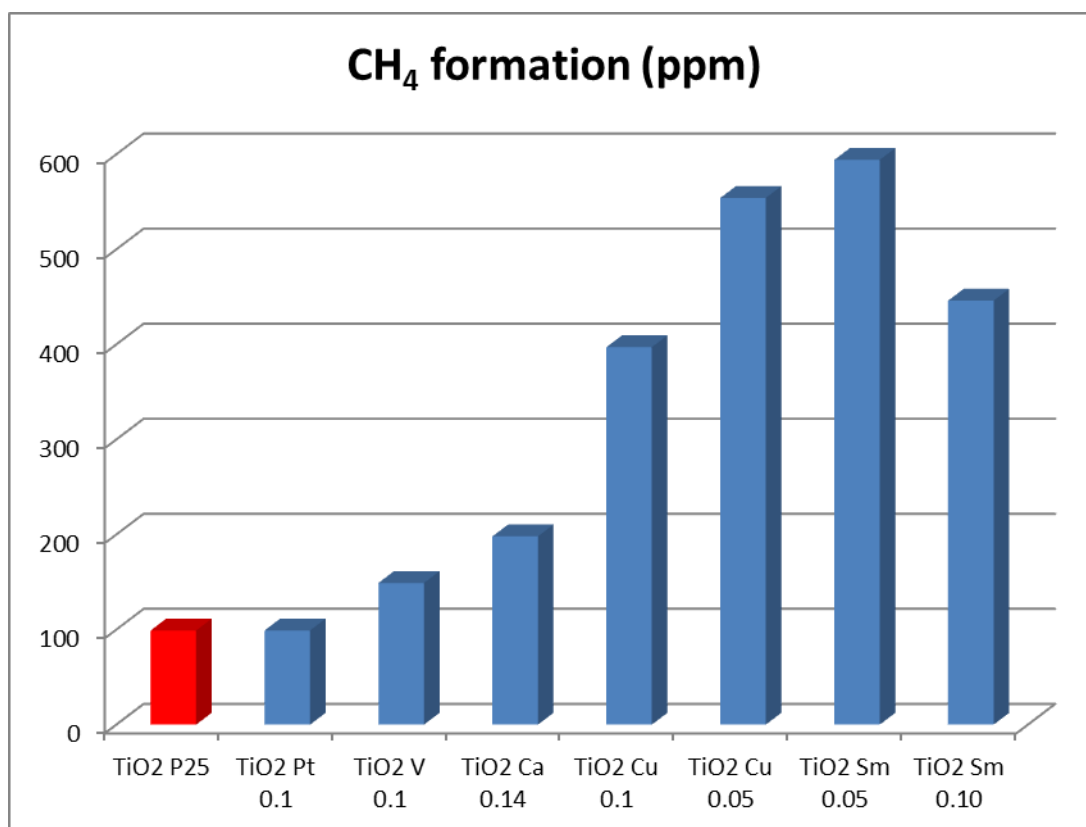


Figure 1. Formation of methane after 14 hours of reaction for several photocatalysts formulations, best results were obtained for the use of samarium at 0.05% wt.

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## Bibliography

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