



Photocatalytic reduction of CO₂ in a batch slurry photoreactor

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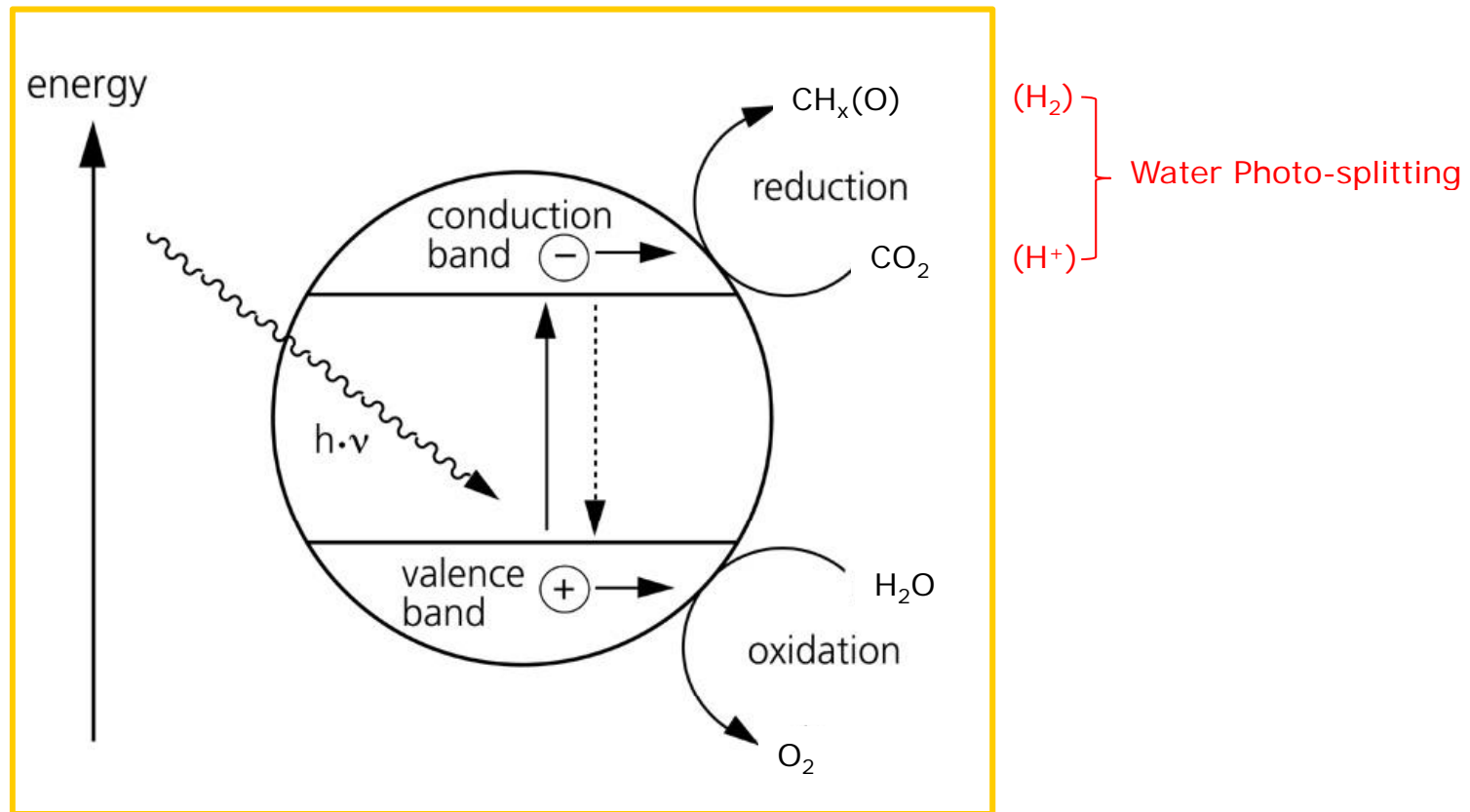
Introduction

- Since the seminal work of **Inoue** et al [1] in **1979**, the photocatalytic reduction of Carbon Dioxide gave rise to a lively interest.
- **Thirty** years have passed since the first publications, the most widely used materials for photocatalysis are still based on **TiO₂**, on systems equipped with artificial UV lamp and using **water** as the source of hydrogen.
- The reported **productivity** are still dramatically **low**, in the order of some **μmol · h⁻¹ · gcat⁻¹**.
- The use of a **scavengers** usually isopropanol, but also inorganic (Na₂SO₃) have been added as well, seems to **reduce recombination** of the couple electron / hole created on the semiconductor by photon adsorption **enhancing yield** of reduction product.
Indeed TiO₂ acts as photo degradation catalysts of organic water pollutant.



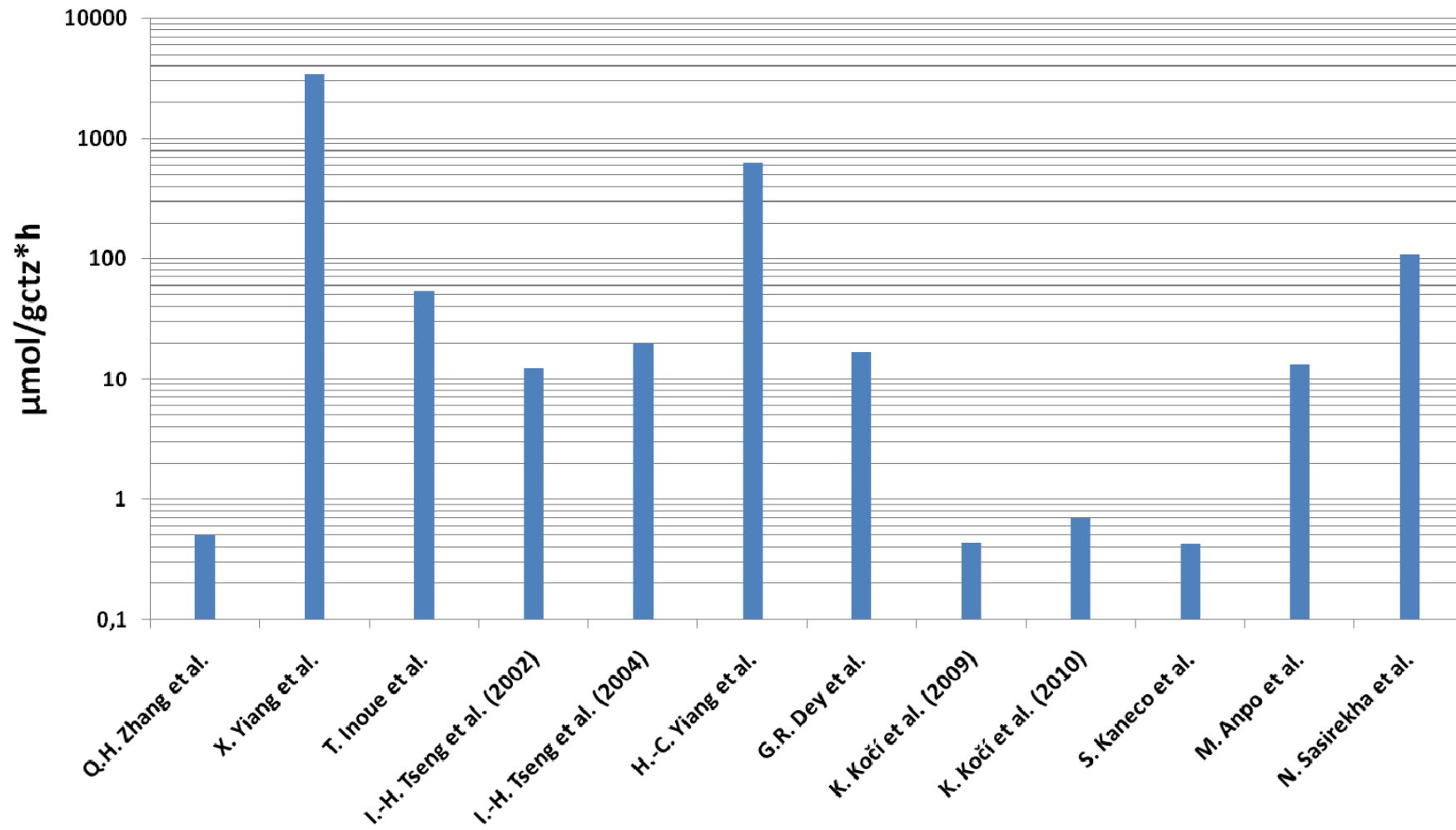
[1] Inoue, T.; Fujishima, A.; Konishi, S.; Honda, K. *Nature* **1979**, 277, 637

System



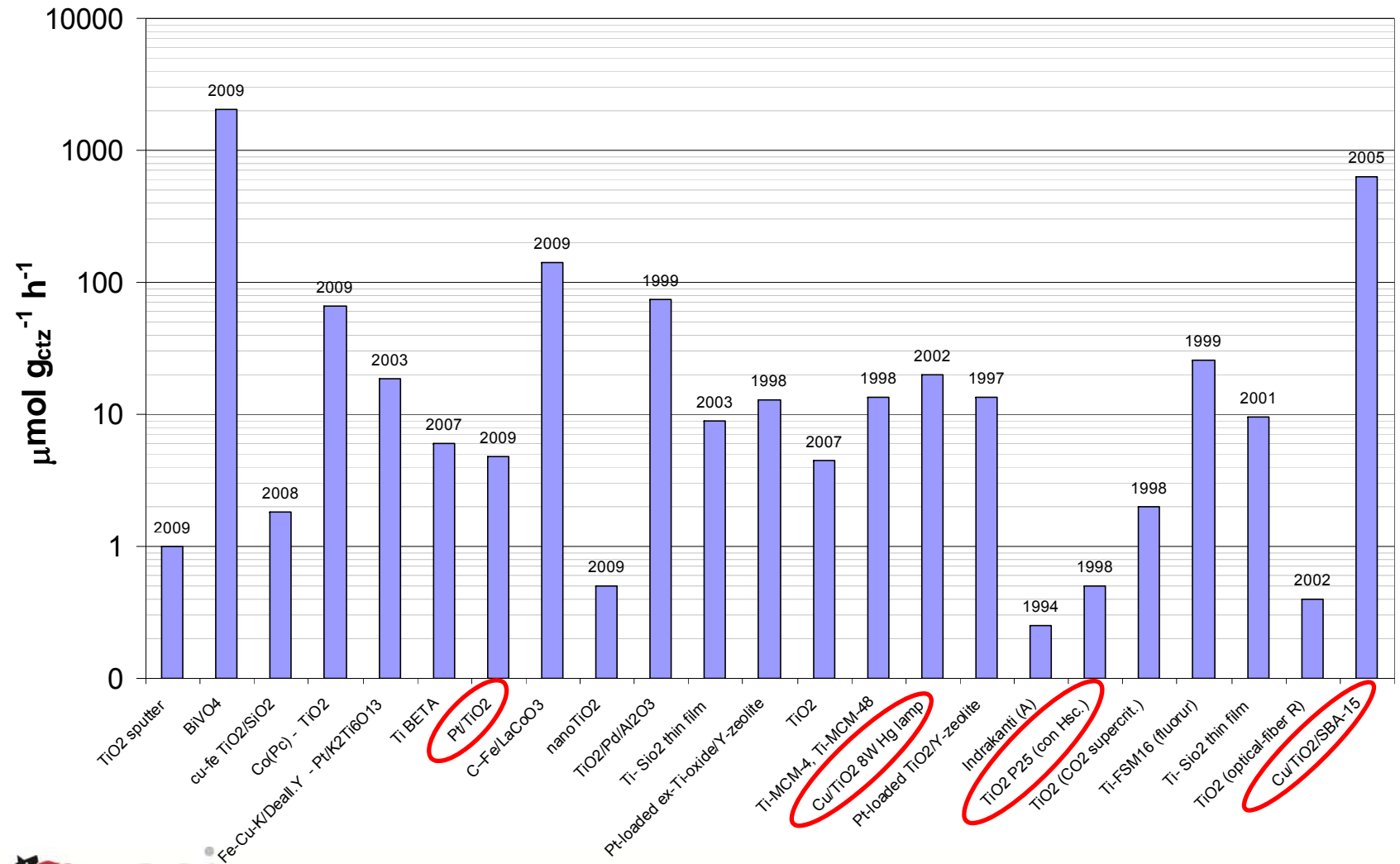
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State of the art



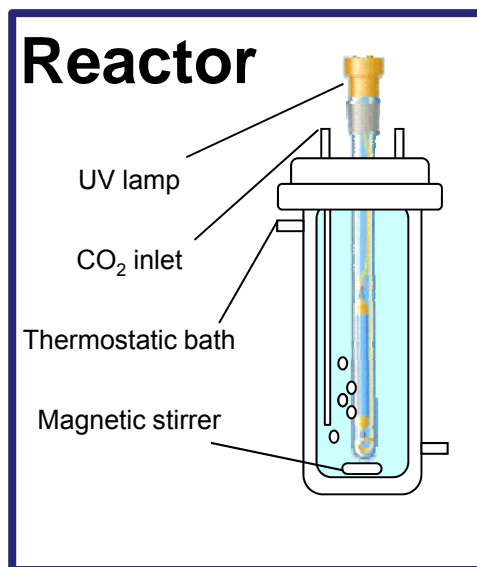
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State of the art

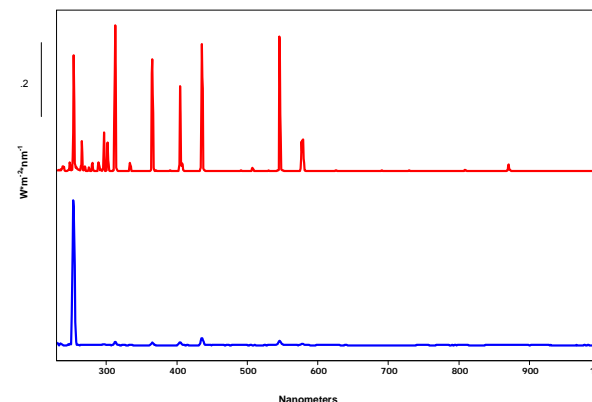


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Experimental setup

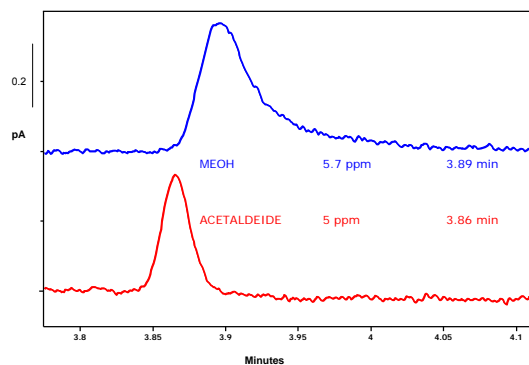


- CO₂ continuously bubbled and circulating
- Thermostatic Double jacket
- Continuous stirring
- Ca. 1 g of catalyst in 0.7 litre
- 20 hour reaction
- Room temperature and pressure



UV high mercury pressure lamp
500W power
(313 nm) 580 μwat/cm²

UV low mercury pressure lamp
17W power
(254 nm) 50 μwat/cm²



Complex hydrocarbon pool not even easy to resolve:

METHANOL and **ACETALDEYDE** overlap on HP-PONA
Propane and **Propene** on HP-PLOT/U
METHANOL and **t-BUTANOL** on FFAP



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Test Results **without** Scavenger

CATALYSTS

DEGUSSA STANDARD TiO₂ P25

P25 2 – 4 % Cu after 5h calcination at 550°C by incipient wet impregnation with **Copper Nitrate**

2%Cu-TiO₂ / SBA-15 (45/55) following Yang et al; Catal Lett (2009) 131,381

(§)



(§) Letterature references:

- a **T. Inoue**: TiO₂ powder , 1g/100ml; 30 h; ambient T and P; lamp 500W high-p. Hg; GC-column, PEG 200 and molecular sieve.
- b **I.-H. Tseng(2002)**: cat. 0.15-0.6 g in 300 ml; 6h; ca. 50°C; 101.3-135.6 kPa; lamp 8W low-p. Hg; GC-column, Porapak Q.
- c **H.-C. Yang (2009)**: Cu/TiO₂/SBA-15 0.05 g in 550 ml; 8h; ca. 42°C; lamp 400W medium-p. met halide; GC-column, Porapak.

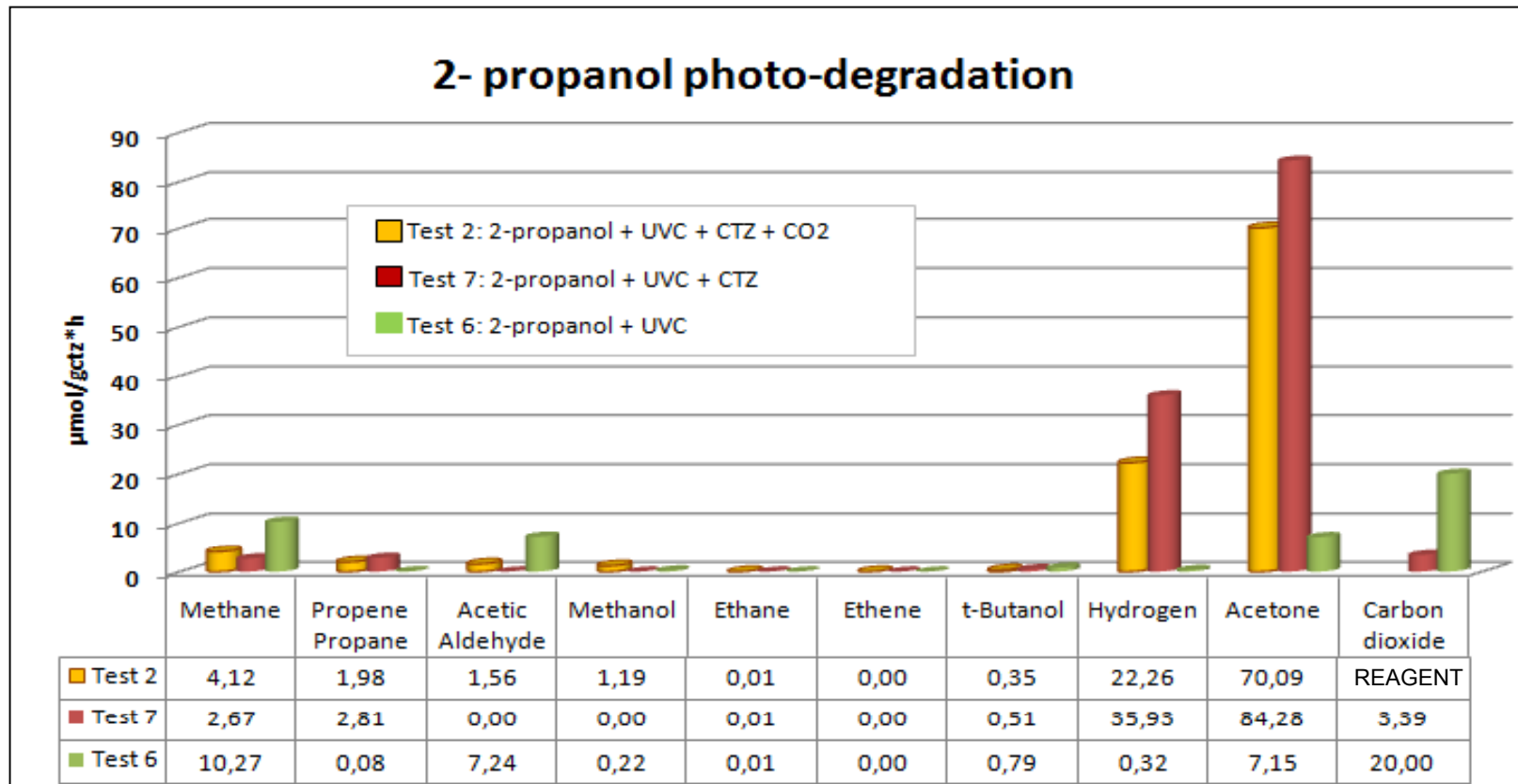


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Test Results **with** Scavenger

Products detected:

hydrogen, methane, acetaldehyde, methanol, acetone, propene/propane, ethane, ethene, tert-butanol.



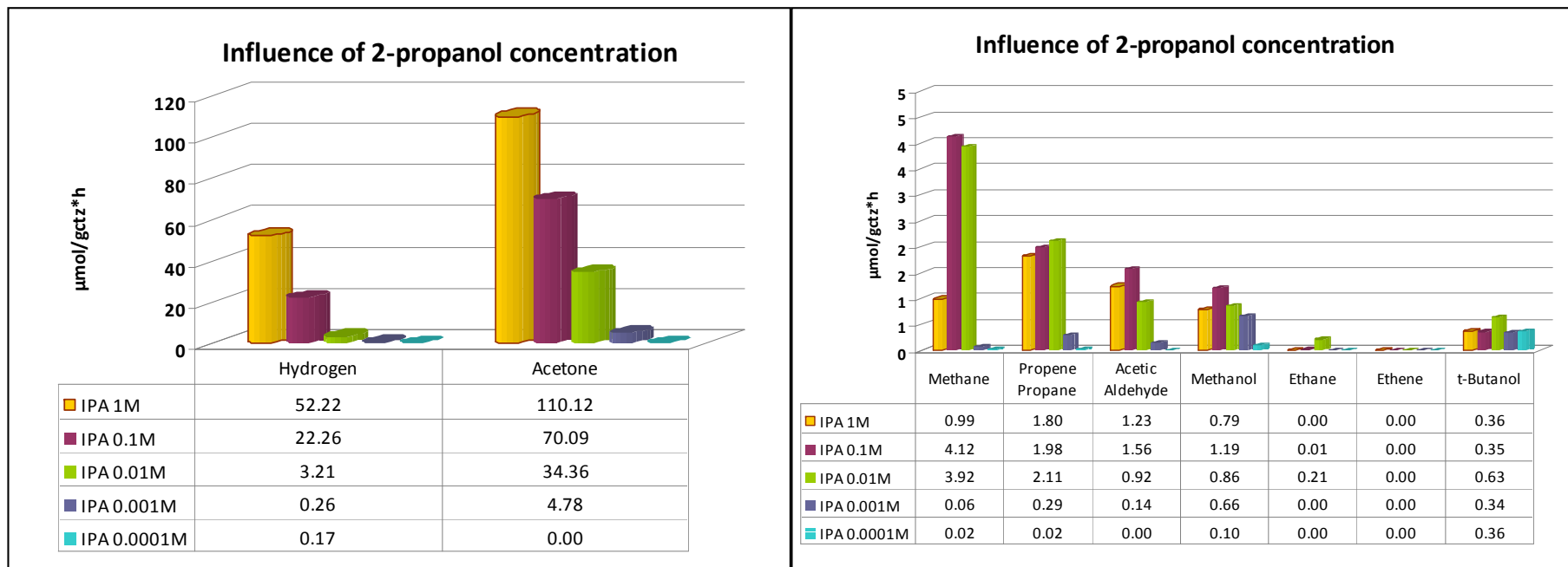
IPA undergo UV- photolysis [*] itself even in absence of CTZ



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[*] Herasymowyachnd, O. S., Knight, A. R. Canadian Journal of Chemistry. 1972, 50, 2217.

Test Results Changing Scavenger Concentration



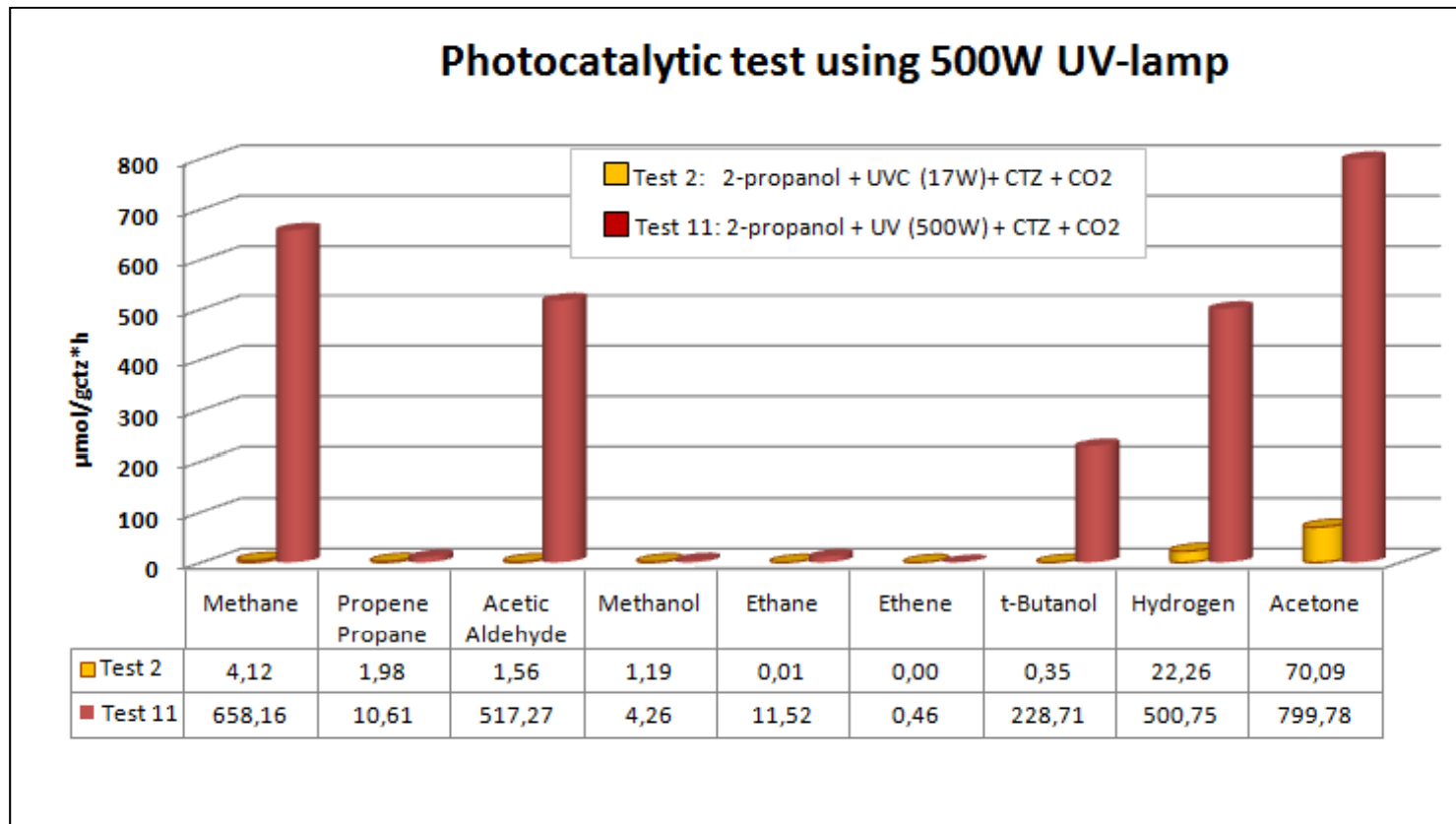
Indeed IPA acts as hole scavenger

Partially oxidized / reduced product follow complex reaction path

Why some product increase with decreasing IPA?



Test Results Changing Power UV-Lamp

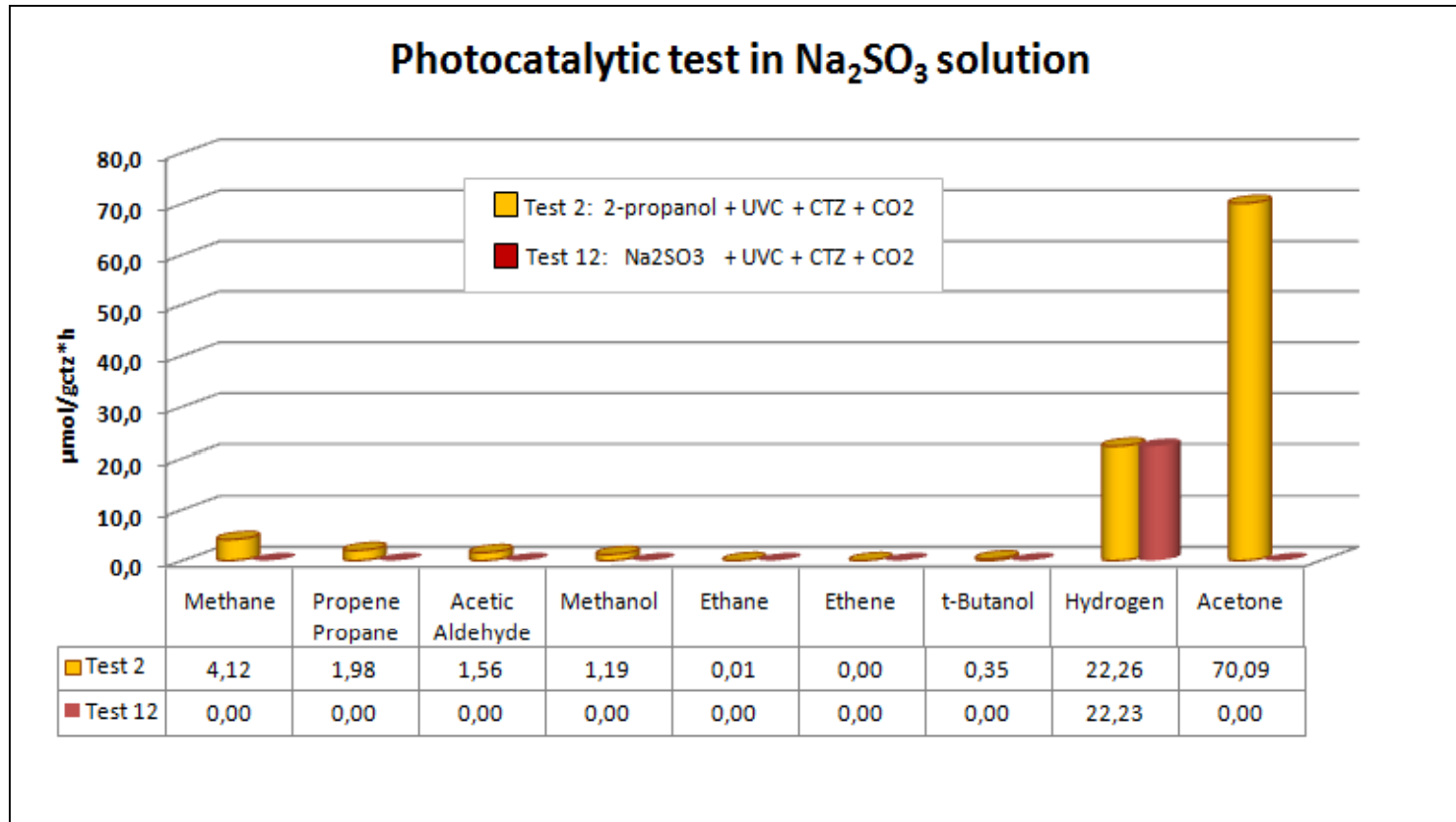


High power lamp greatly enhance typical photolysis product



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Test Results **with Inorganic Scavenger**

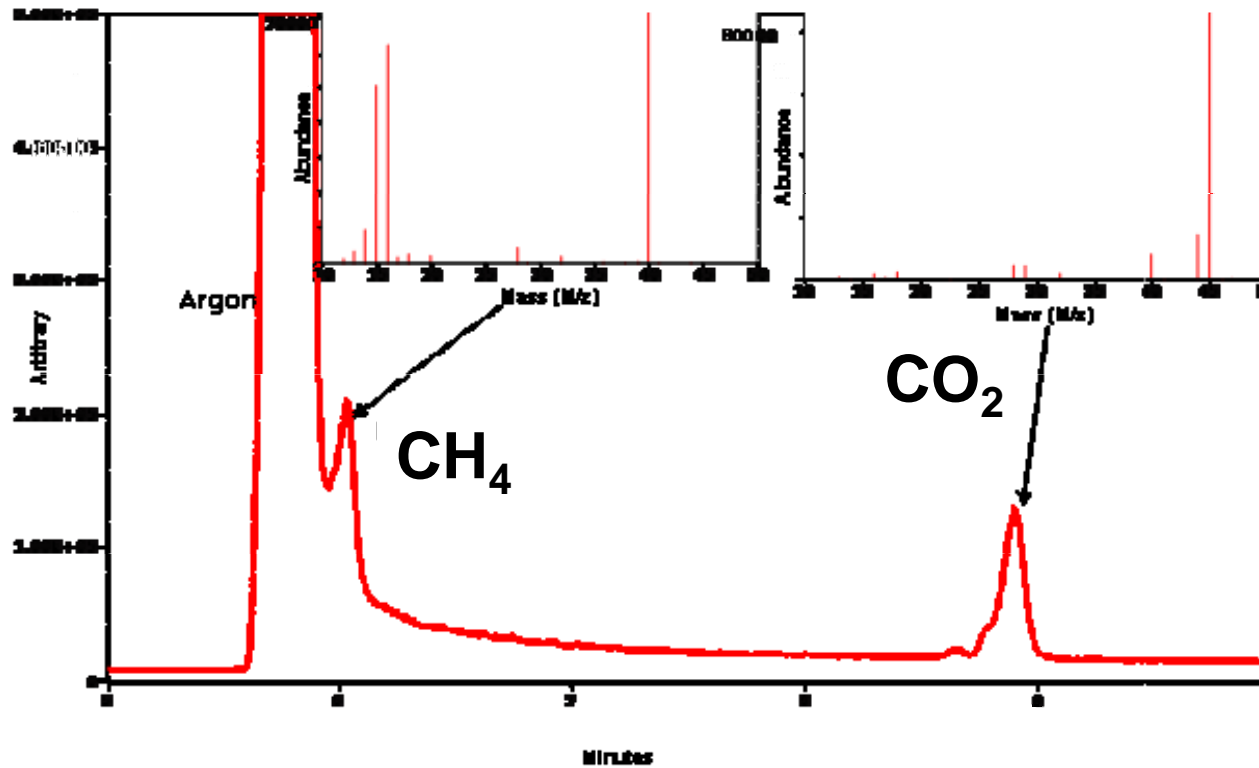


With Inorganic scavenger only water splitting is detected



Test Results with Labelled CO₂

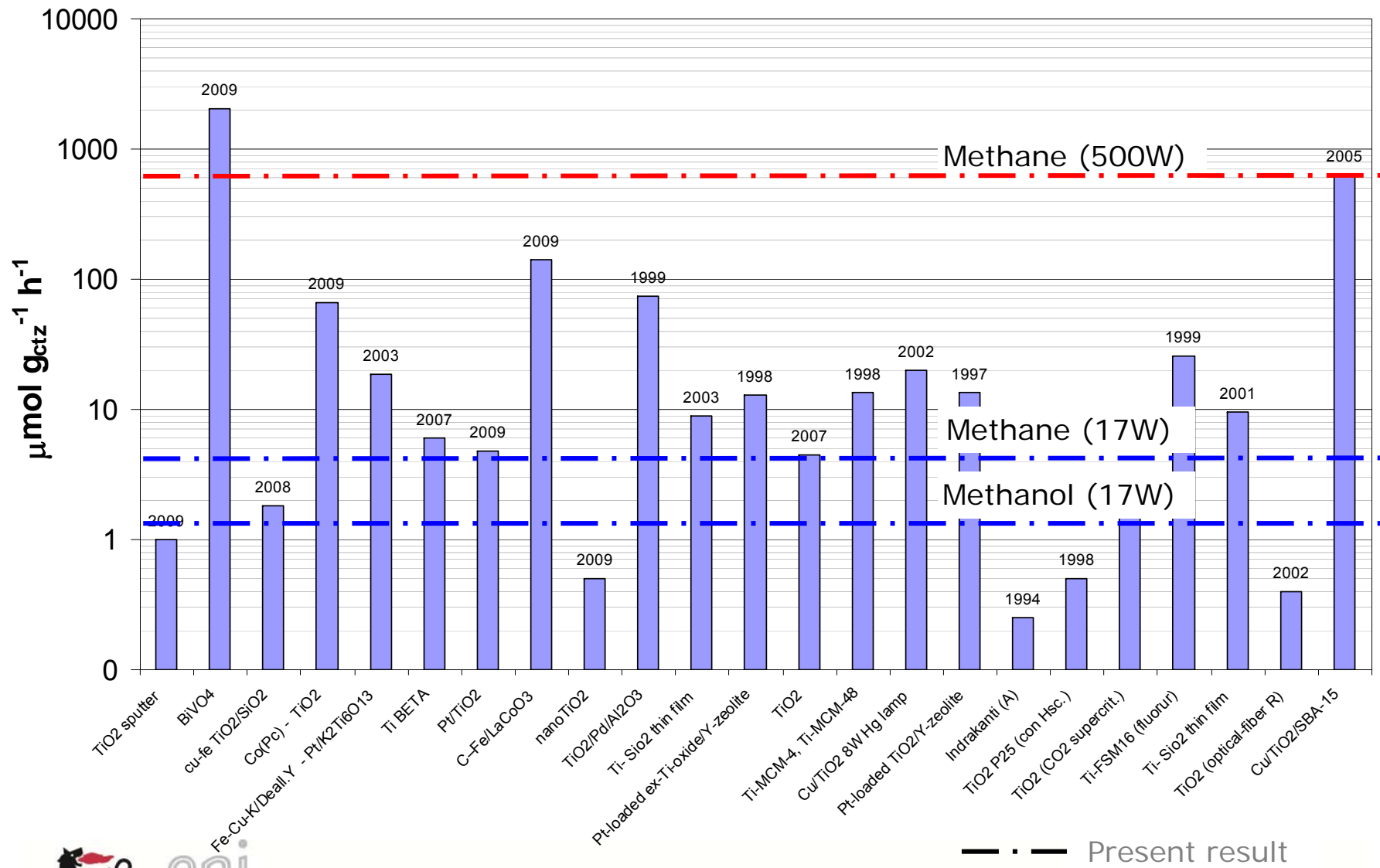
May IPA still have a role as H₂ carrier in CO₂ hydrogenation?



¹³C labelled CO₂ was used to rule out the origin of partially oxidised product



State of the art / present result



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Conclusion

- In no case the presence of labelled ^{13}C could be detected in partially oxidized products overcoming the natural abundance.
- In our experimental condition, we have no evidence that CO_2 could show even partial photo induced reduction by means of Cu doped titania catalysts.
- Use of labelled $^{13}\text{CO}_2$ is, probably, the lonely way to be confident in the identification of Carbon Dioxide photoactivation
- Other approaches, also by using accurate blank experimental design, can be blinded by pollution from the environment or from the catalytic system

