Radiocatalytic and Photocatalytic Oxidation of Organics, and Reduction of Cationic Metals and Water

Y. Su, Y. Wang, M. A. Henderson, T. B. Fryberger*,
Y. Liang, J. L. Daschbach, and C. H. F. Peden

Interfacial and Processing Sciences
Environmental Molecular Science Laboratory
Pacific Northwest National Laboratory
Richland, WA 99352

Funded by: DOE/Environmental Management Science Program

* **Now with Brookhaven National Laboratory**

Background

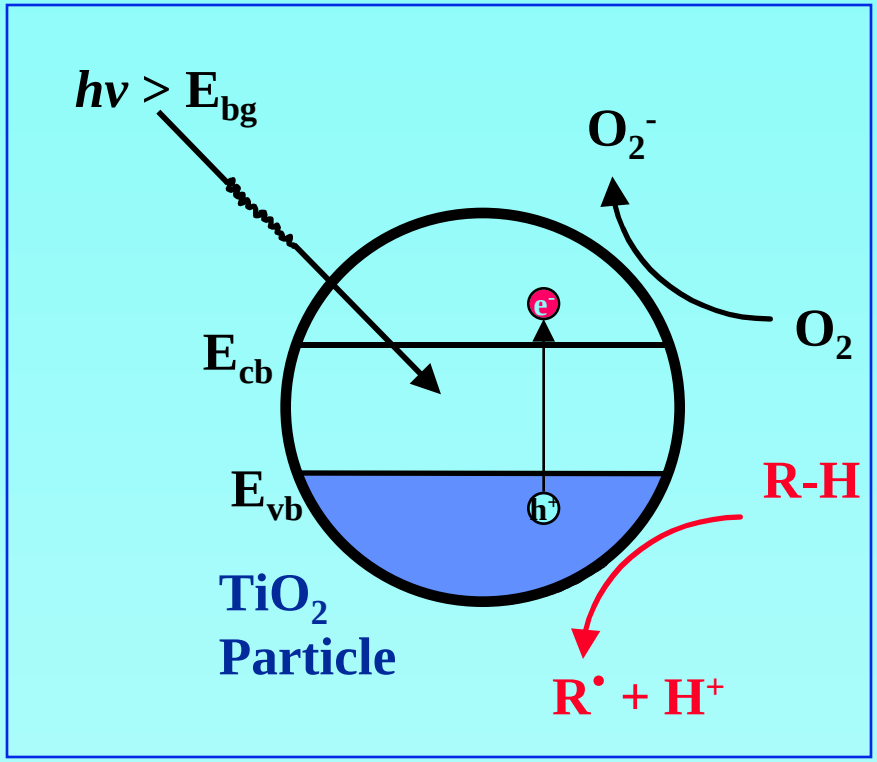
- **Significant amounts of organics (solvents, extractants, complexing agents) exist in waste tanks within DOE sites; these pose several safety and pretreatment concerns.**
  - **a). Safety:**
    - **— toxicity and flammability hazards**
    - **— as reductant in highly energetic and potentially explosive reactions with oxidants.**
  - **b). Pretreatment:**
    - **— chelating or binding agents for radioactive ions, preventing their removal from tank waste.**

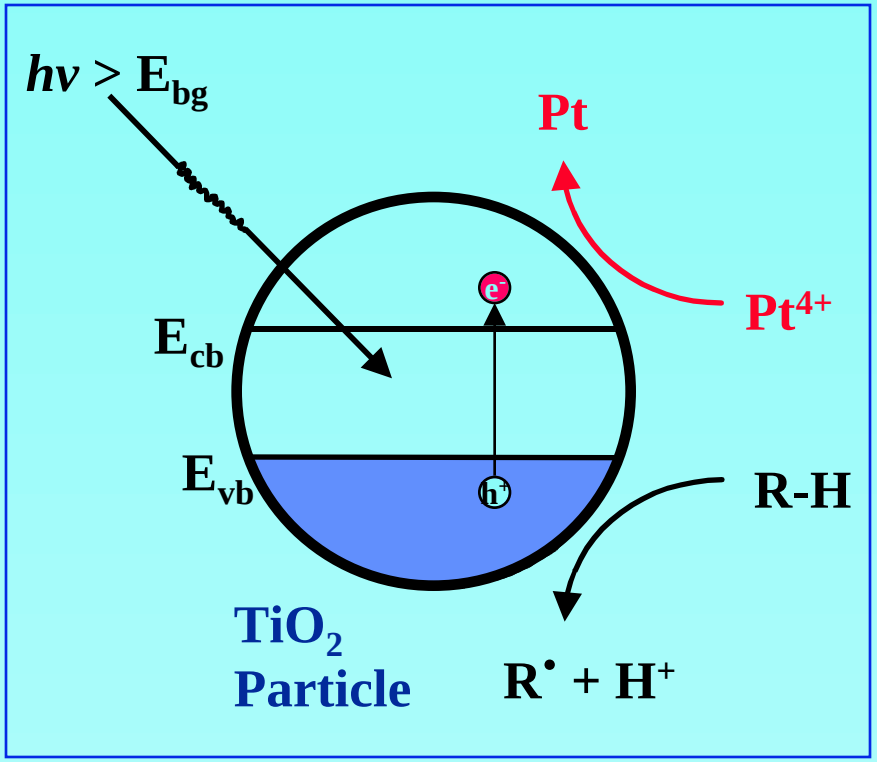
- **Remediation technologies are needed for reducing problem organics without resulting in toxic or flammable gas emissions, and without requiring thermal treatments.**

Objective

- **Investigate feasibility and mechanism of ionizing radiation induced radiocatalysis on stable, wide bandgap semiconductor catalysts.**
- **This is a novel approach potentially useful for:**
  - **oxidation of organics**
  - **reductive precipitation of metals and oxides**
  - **understanding tank waste aging and radiation-induced damage in solids**

UV Photocatalysis on Colloidal Semiconductor Particles

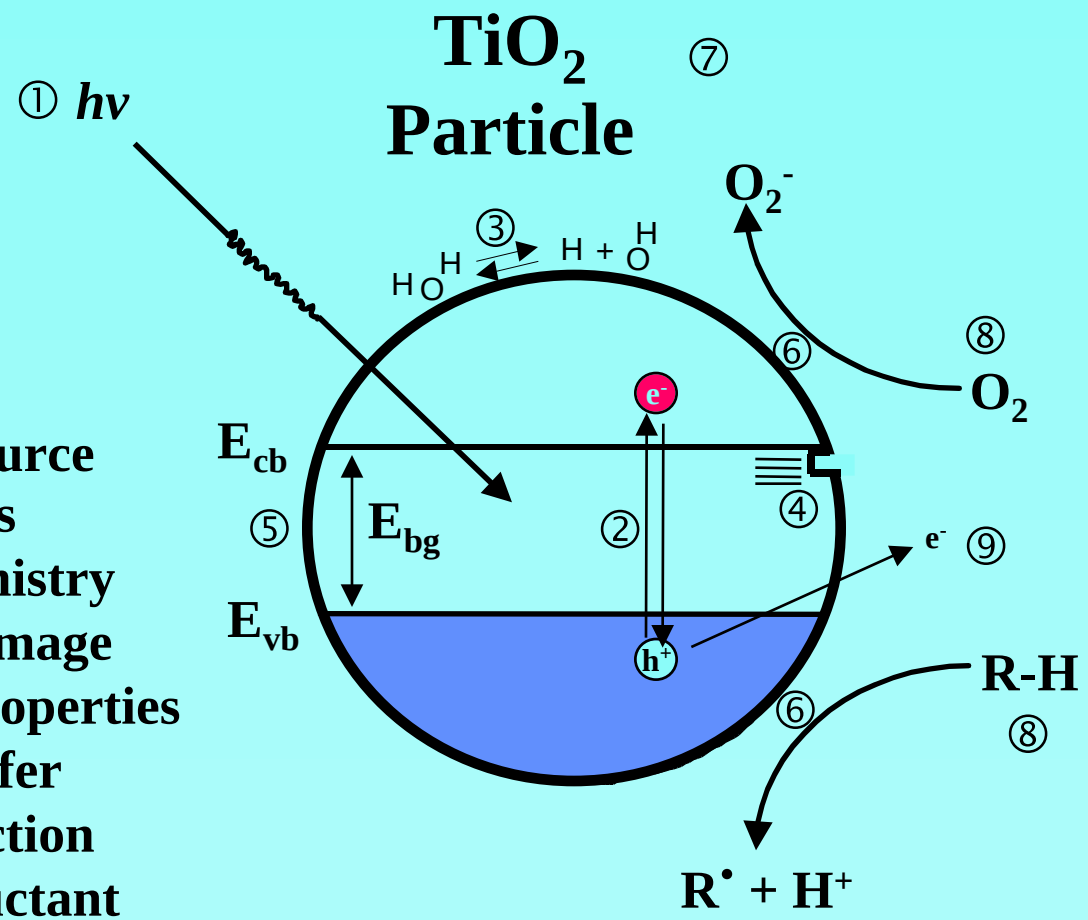




- **Oxidation of Organics**
- **Reduction of Metal Cations**

- **Electron-Hole Pair Mechanism**

Critical Science Issues in Radiocatalysis



① excitation source
② e^-/h^+ lifetimes
③ surface chemistry
④ radiation damage
⑤ electronic properties
⑥ charge transfer
⑦ catalyst selection
⑧ oxidant/reductant
⑨ secondary electrons

Radiocatalysis

Radiolysis

$H_2O \rightsquigarrow OH\bullet, e_{aq}^-, H\bullet$

e^-–h^+ Catalysis (photocatalysis)

$TiO_2 \rightsquigarrow e^- + h^+$

$(h^+ + OH^- \longrightarrow OH\bullet)$

OH• Radical (or h^+) Mediated Reactions

Oxidation of Organics, Reduction of Metal Ions, etc.

Product Identification (Reaction Mechanisms)

- **Conceptually this is an extension of the UV photocatalysis process**

Approach

Gamma Radiocatalysis and UV Photocatalysis:

1). Oxidation of Organics:
EDTA + TiO_2 (O_2, pH, Sr^{2+})

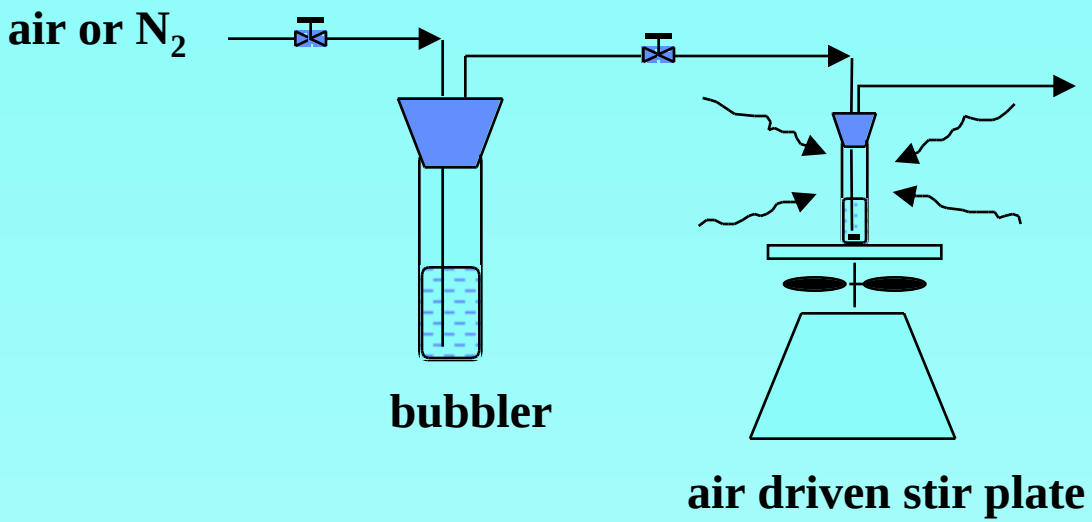
2). Water Cleavage into H_2:
Formic acid + Pt/TiO_2

3). Reduction of Metal Cations:
Formic acid + H_2PtCl_6 + TiO_2

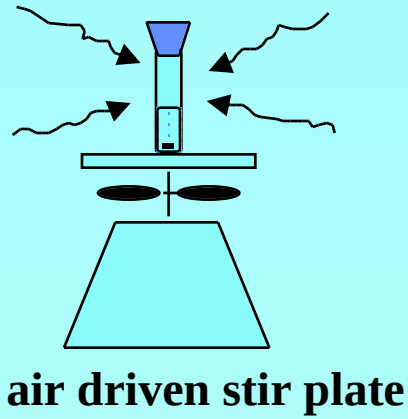
Experimental Conditions

- **Substrate:** 1). 0.02M aqueous EDTA solution
  2). 0.1M Formic acid
  3). 0.5wt% H_2PtCl_6 solution
- **Catalysts:** 1) 0.01 ~ 0.1 g/ml TiO_2 (Degussa P-25)
  2) 0.01 ~ 0.1 g/ml 0.5wt%Pt/TiO_2
- **γ Irradiation:** 1~ 7 MRad from ^{60}Co source
  (solutions continuously stirred to suspend TiO_2)
- **UV Radiation:** 100 w Mercury Lamp
- **Analysis:** GC, GC/MS, HPLC, IC

Experimental Setup

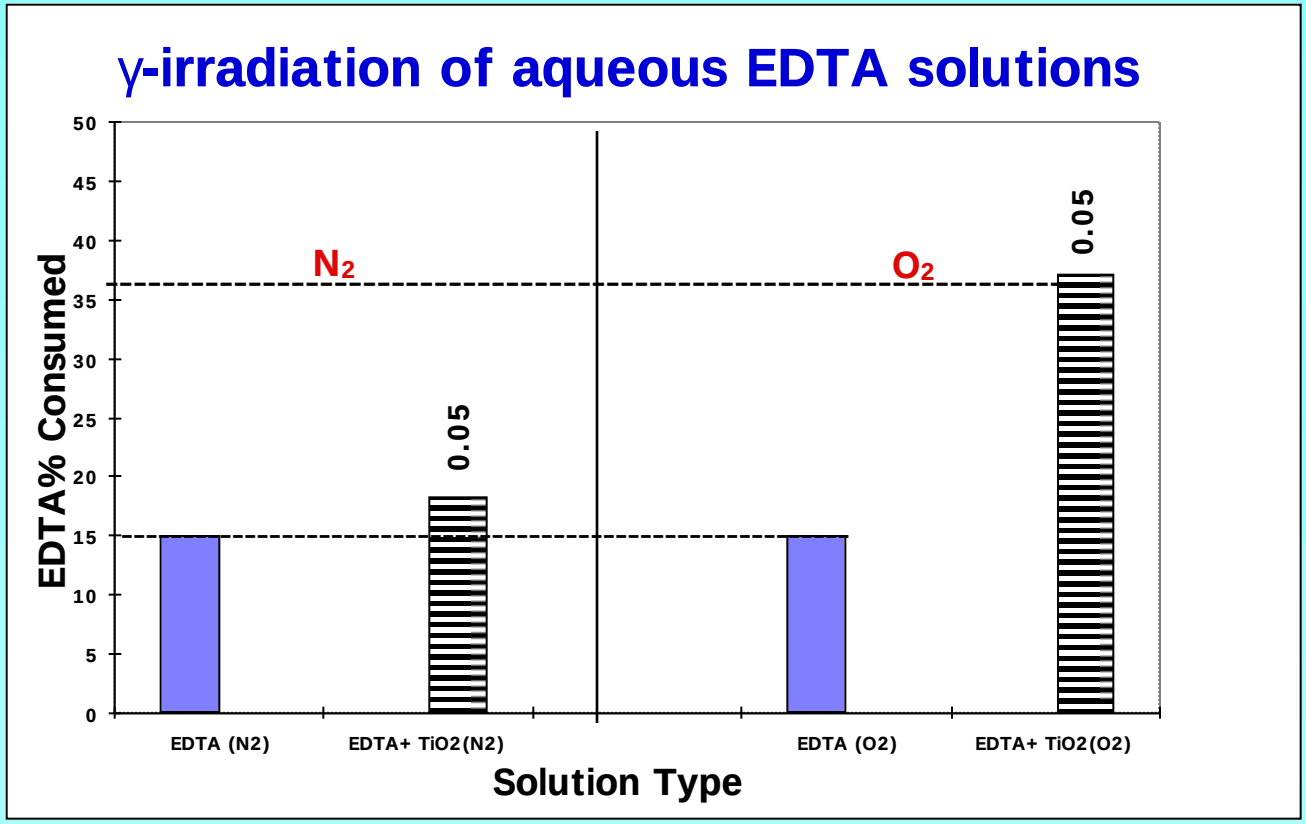


(a) gas flowing system



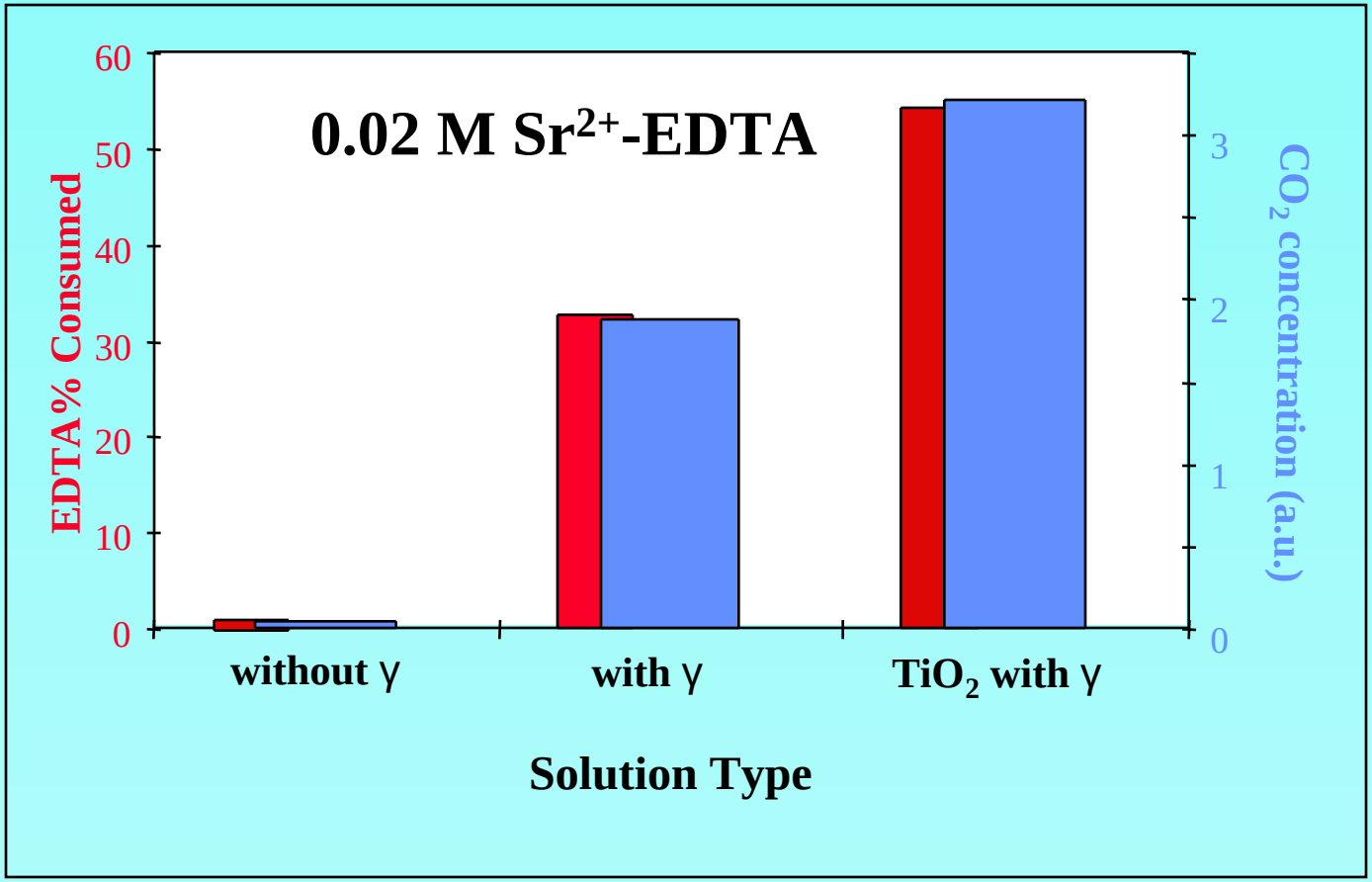
(b) static gas system

O_2 Effect on Oxidation of EDTA



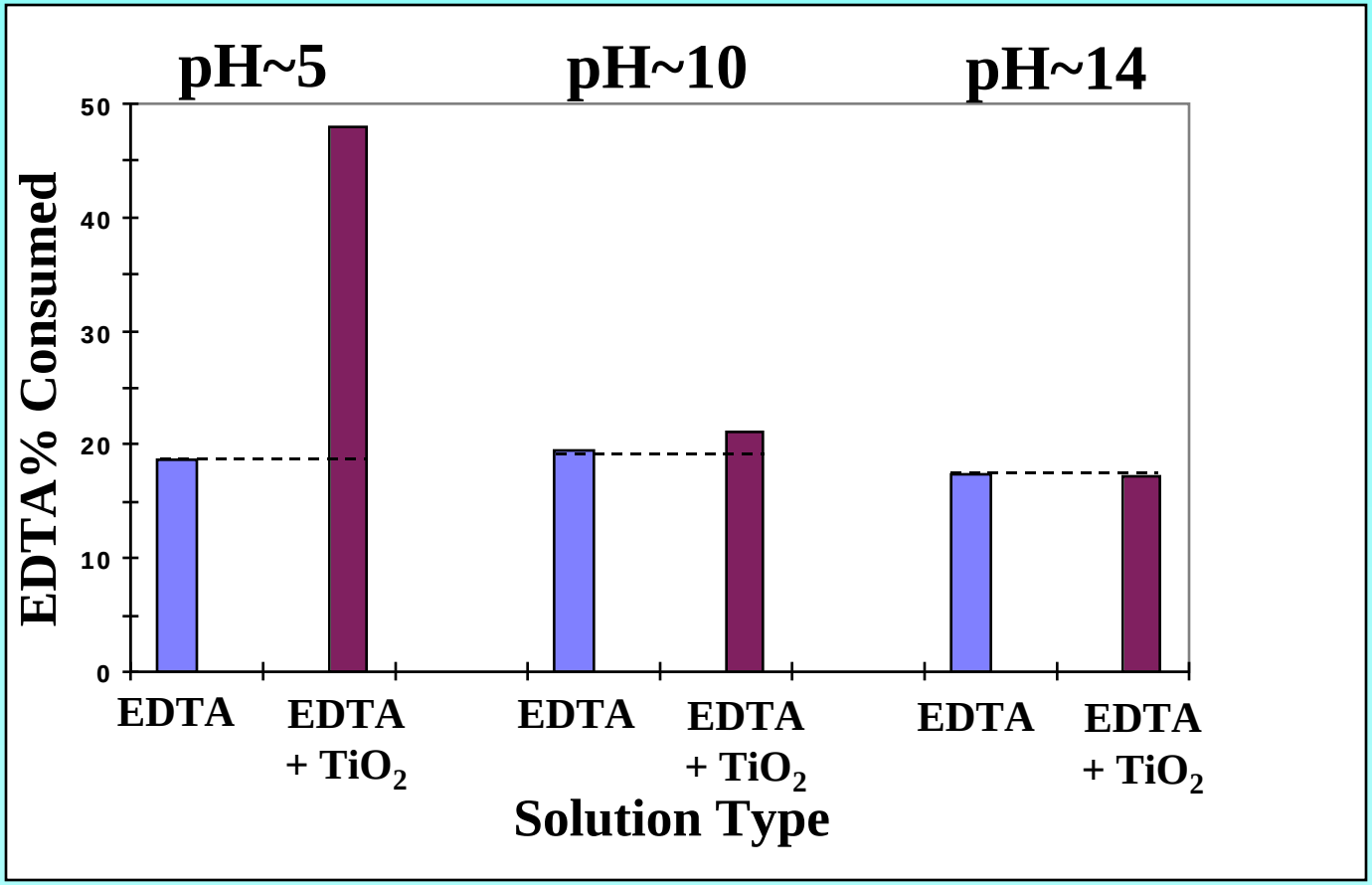
- O_2 plays a key role (scavenge electrons) on the oxidation of EDTA in TiO_2 suspension.
- TiO_2 doubles the rate of EDTA oxidation.

CO_2 Production from EDTA Oxidation



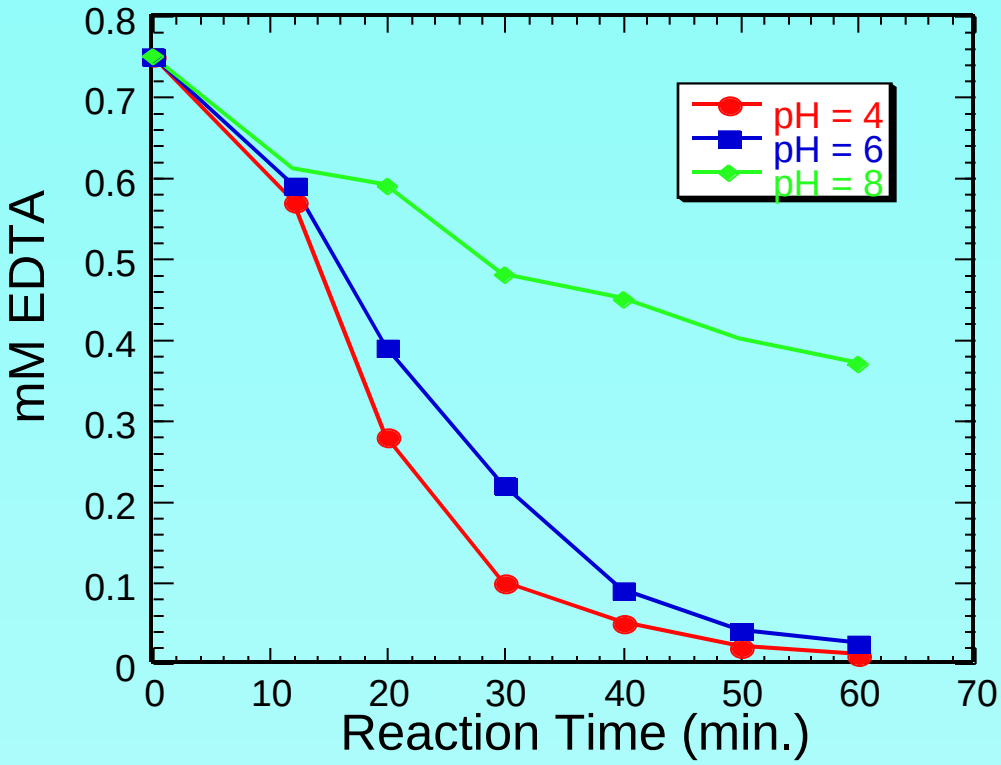
- CO_2 formation tracks EDTA Oxidation.

pH Dependence of EDTA Oxidation



- **No TiO_2 promotion of EDTA Oxidation at high pH.**

pH Dependence of EDTA Oxidation for UV Photocatalysis

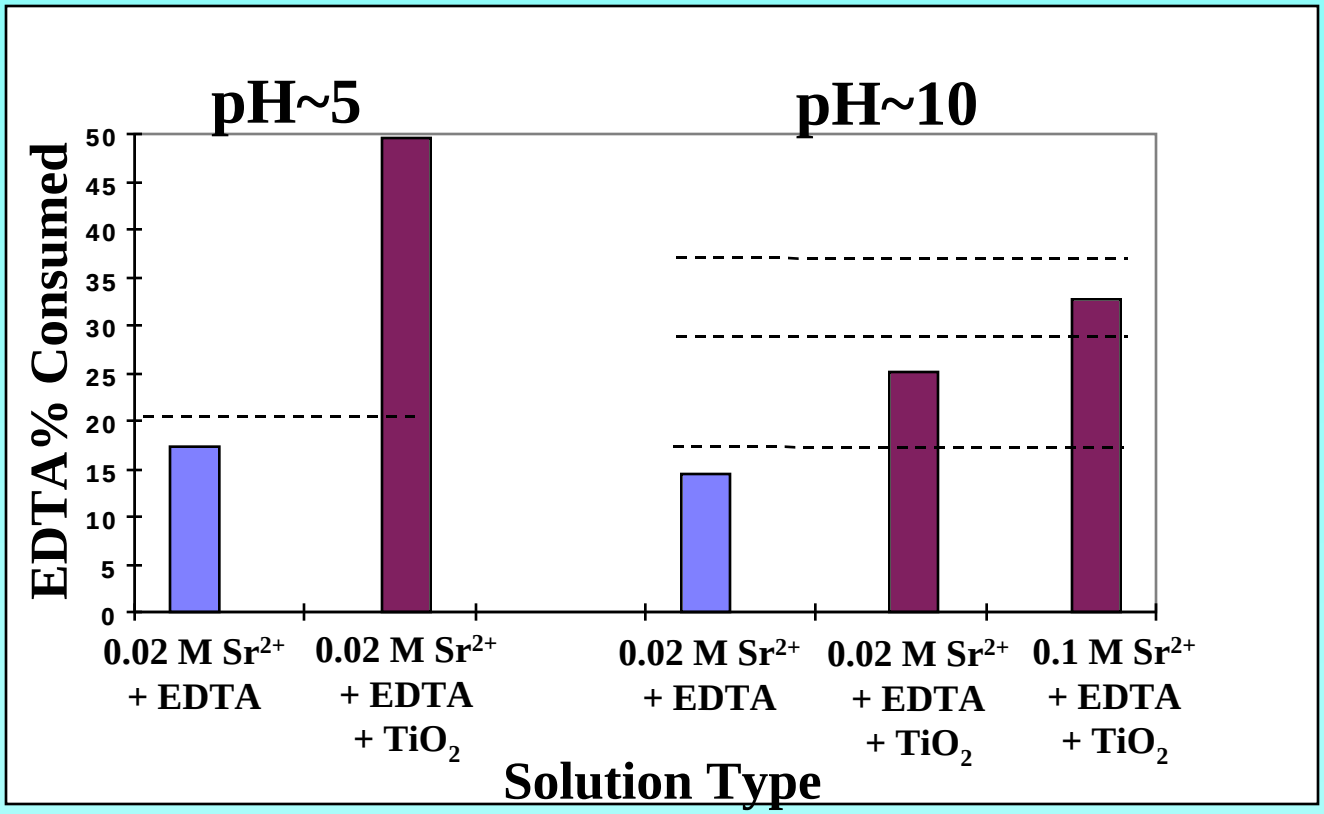


- **Reaction rates decrease dramatically at pH's above the isoelectric point of TiO_2.**

Datye, *et al.*, ES&T 31 (1997) 3475

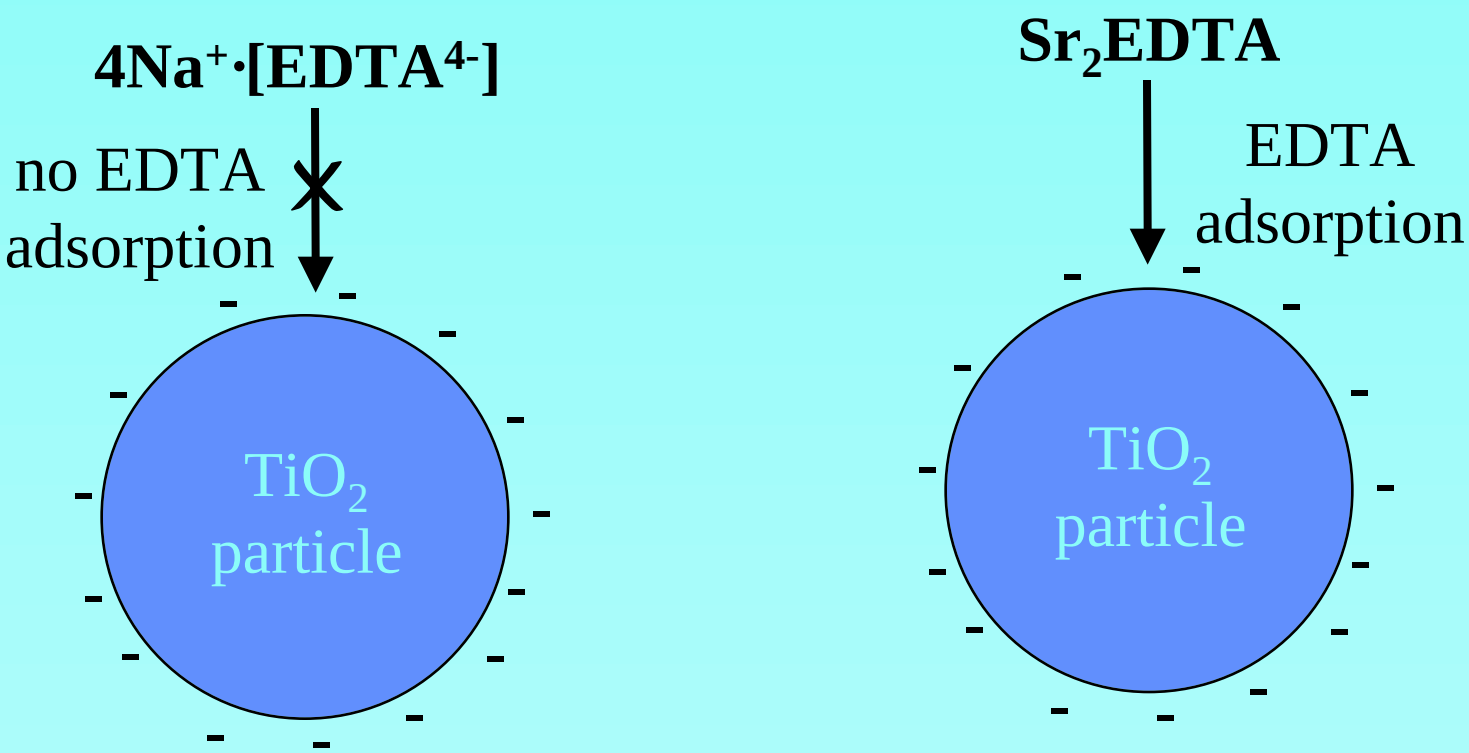
- **pH dependence in radiocatalysis matches that observed in UV photocatalysis**

pH Dependence of Sr^{2+}/EDTA Oxidation



- **Complexing EDTA removes much of the pH effect.**
- **Complexing agents bound to radionuclei (e.g. ^{90}Sr) can be destroyed at high pH.**

Model for Radiocatalysis of Complexed EDTA at High pH



- **Neutral species (such as complexed EDTA) are not repelled from the negatively charged TiO_2 surface at high pH.**

Summary

- **The Oxidation of organics (EDTA) in the presence of TiO_2 and γ irradiation at pH~5 increase up to 2 times.**
- **TiO_2 promotion of SrEDTA oxidation at pH~ 10 because neutral species are not repelled from the negatively charged TiO_2 surface.**
- **Similarities of Radiocatalysis with UV photocatalysis have been observed suggesting that e^-/h^+ processes are important.**

Preliminary Studies of TPB Degradation: Potential Effects of Titanates and Zero-Valent Noble Metals

Background

- An in-take precipitation process is used at Savannah River to prepare high-level waste for vitrification.
- The process uses sodium tetraphenylborate (NaTPB) to precipitate radioactive Cs in strongly alkaline aqueous media.
- NaTPB decomposition to produce dangerously high levels of benzene has been observed during operation.

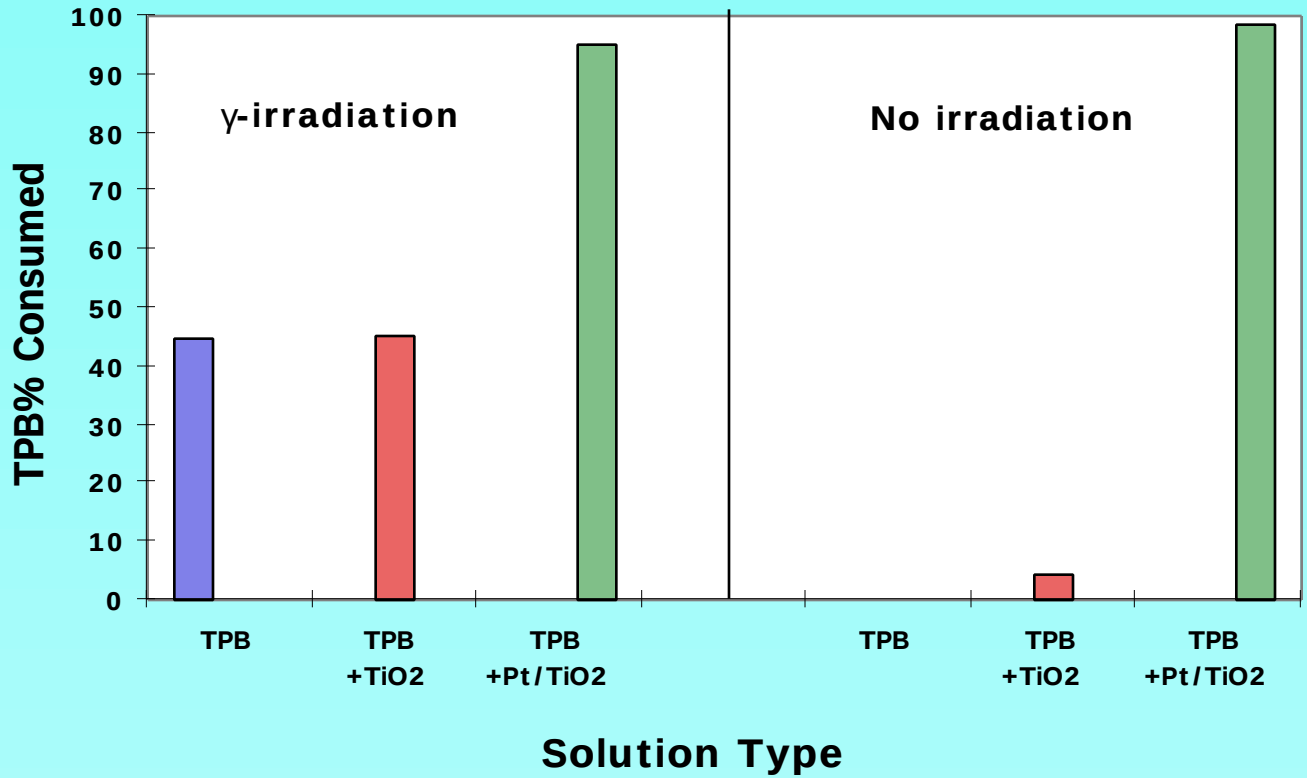
Focus of These Studies

- **Effects of TiO_2 and Pt/TiO_2, with and without γ-irradiation, on the degradation of NaTPB in solution.**
- **Kinetic studies of noble metal effects on the degradation of NaTPB in solution.**
- **Radiation-enhanced reductive precipitation of noble metals on TiO_2 .**

Experimental Conditions

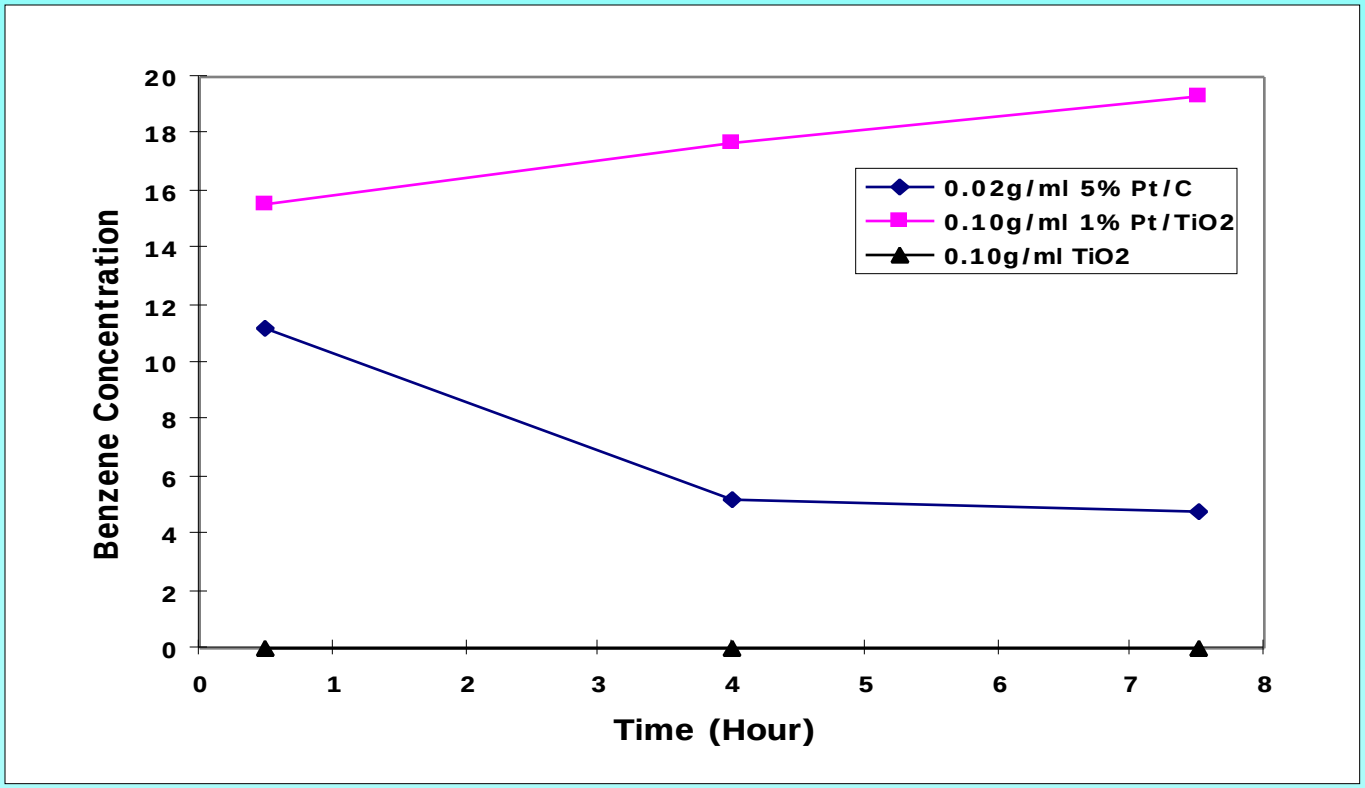
- **Substrate:** 0.02M aqueous NaTPB solution
- **Catalysts:** 1) 0.1 g/ml TiO_2 (Degussa P-25)
  2) 0.1 g/ml 1%Pt/TiO_2
  3) 0.02 g/ml 5%Pt/C
- **γ Irradiation:** ~ 4.2 MRad from ^{60}Co source.
- **Analysis:** HPLC (C18 column) with UV detection at 210 and 265 nm

Degradation of NaTPB in Solution



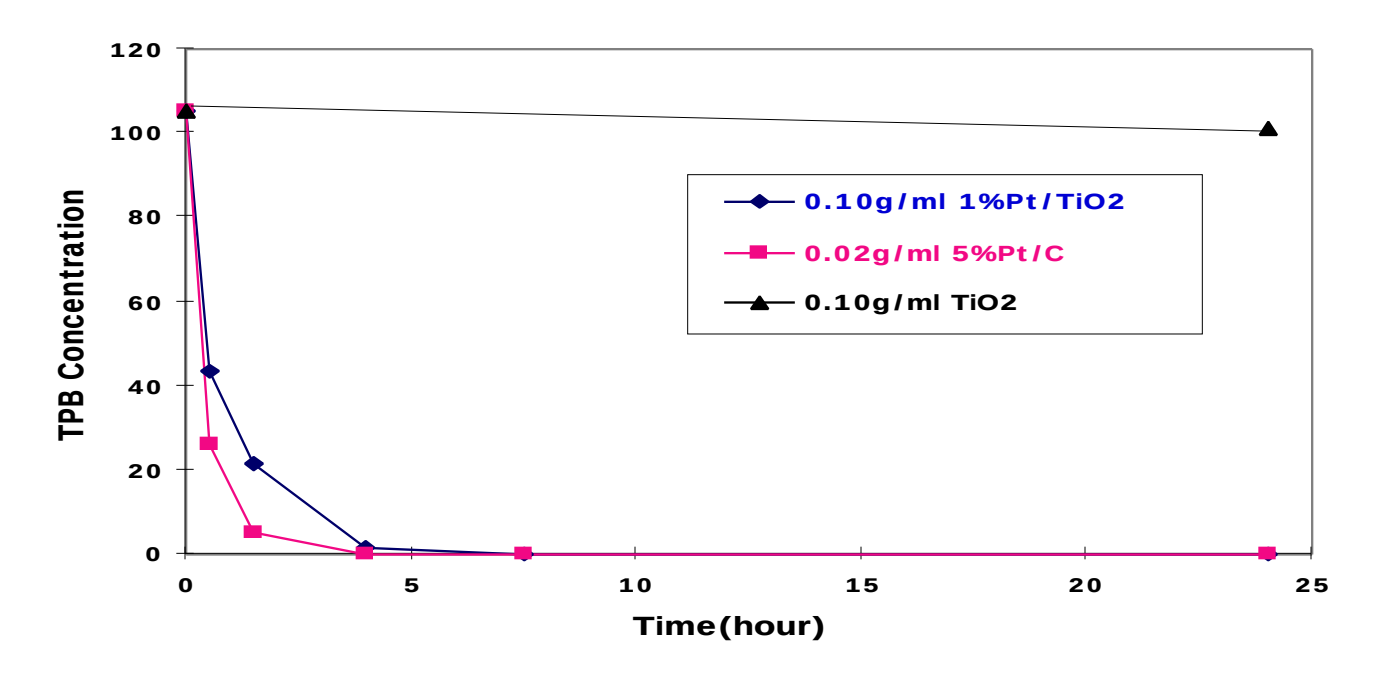
- TiO_2 alone does not effect the rates of TPB degradation in solution.
- However, Pt/TiO_2 significantly promotes degradation of TPB in solution, even in the absence of γ-radiation.
- Benzene is a major product of TPB degradation.

Kinetics of benzene production in NaTPB solution *without* γ-irradiation



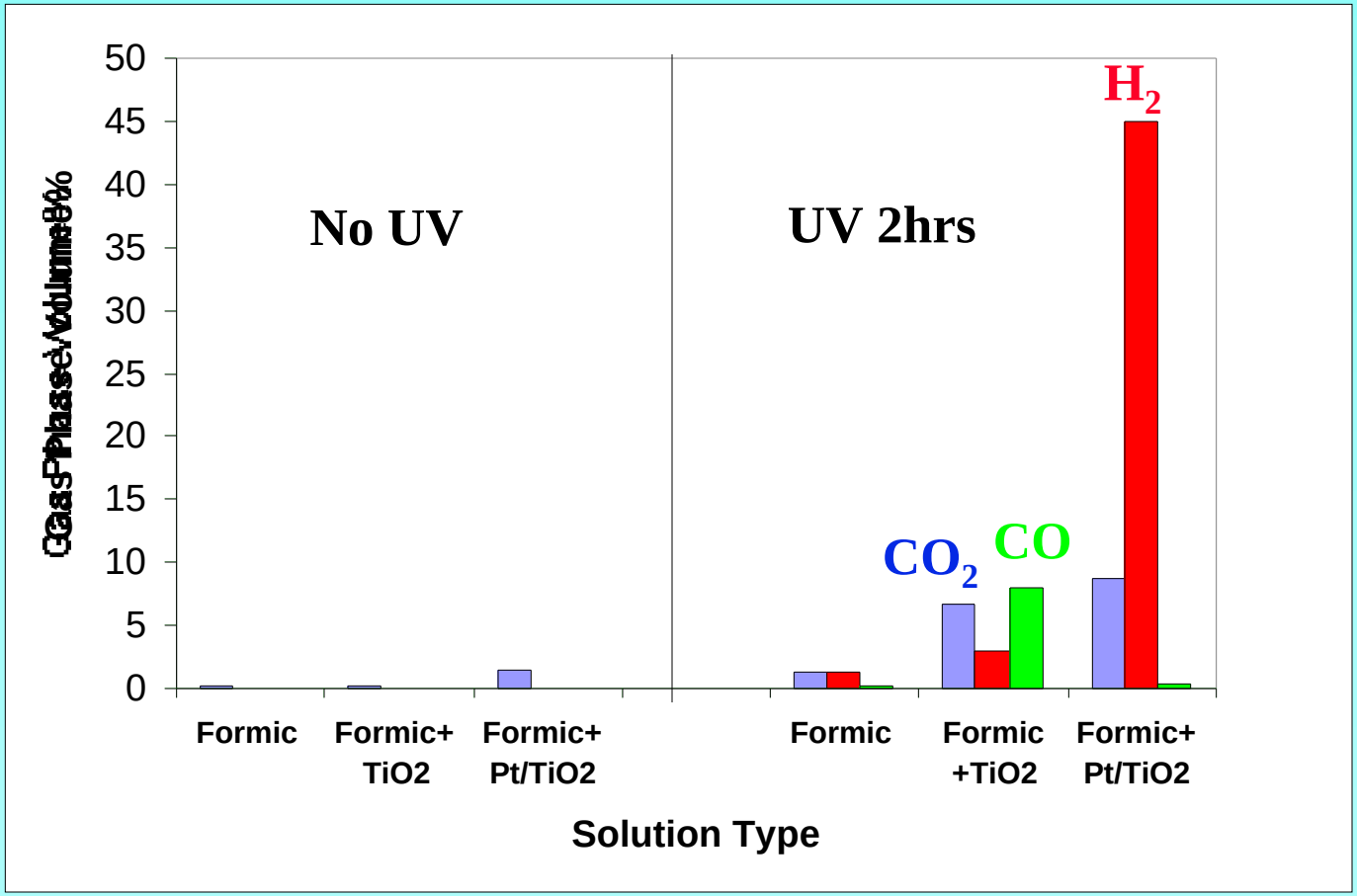
- **Benzene is a major product of TPB decomposition in our studies.**

Kinetics of NaTPB degradation in solution *without* γ-irradiation



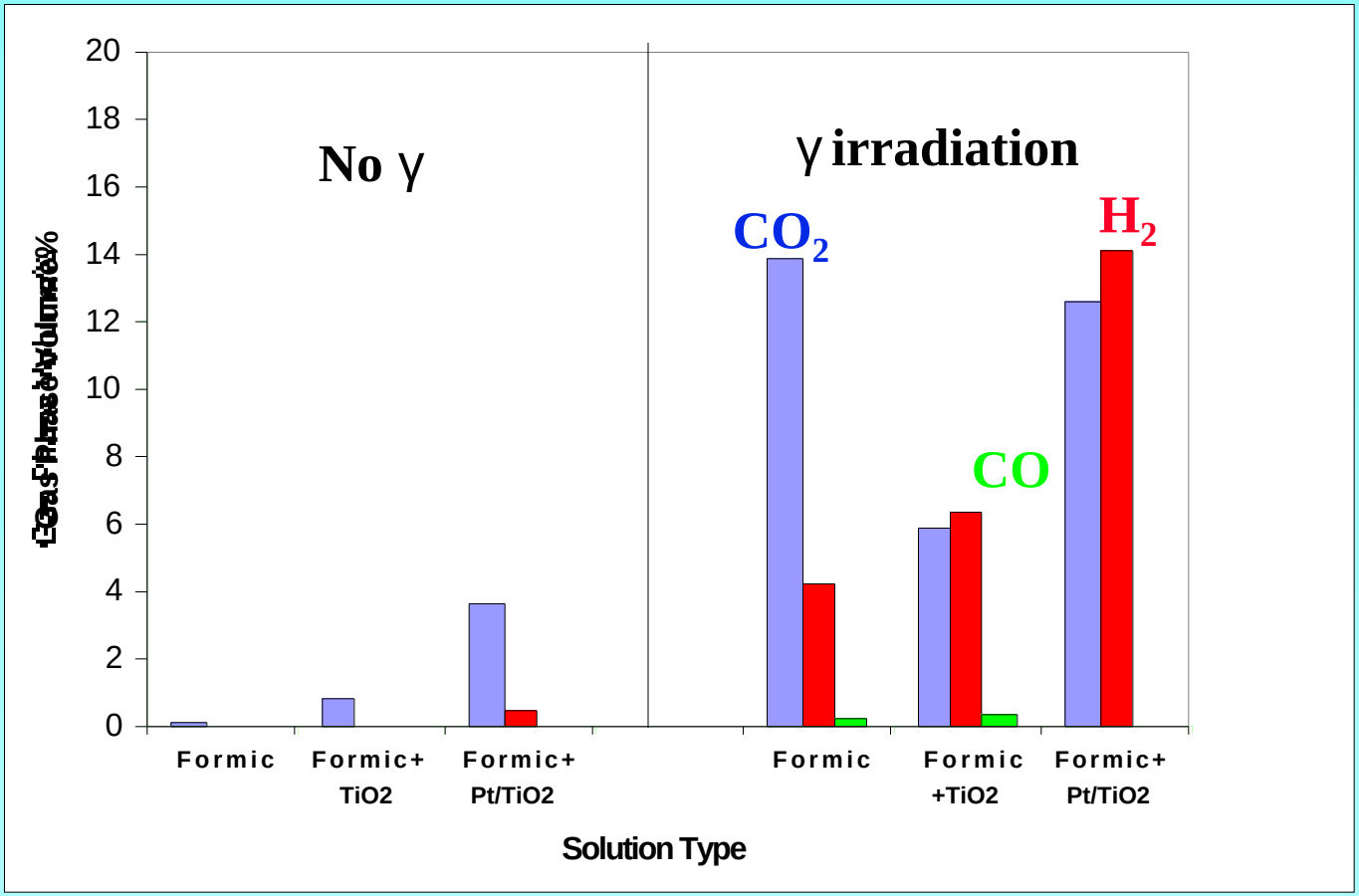
- **Pt metal plays a key role on the degradation of TPB in solution.**
- **Pd metal would be expected to behave very similarly due to its nearly identical behavior for a number of hydrocarbon reactions that are catalyzed by precious metals.**

UV Photocatalysis: H_2 Production



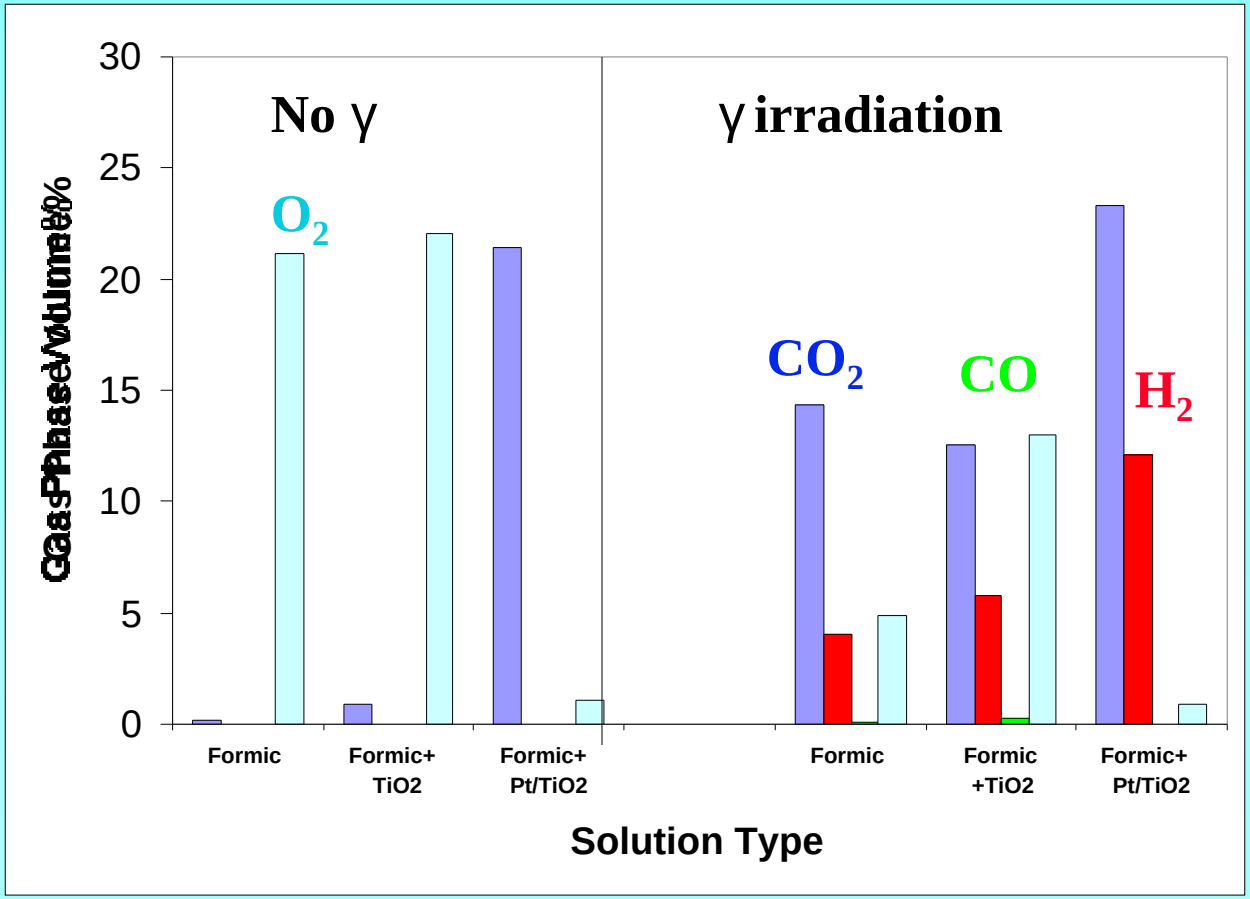
- **Water cleavage into H_2 in the presence of Pt/TiO_2**

γ Radiocatalysis: H_2 Production



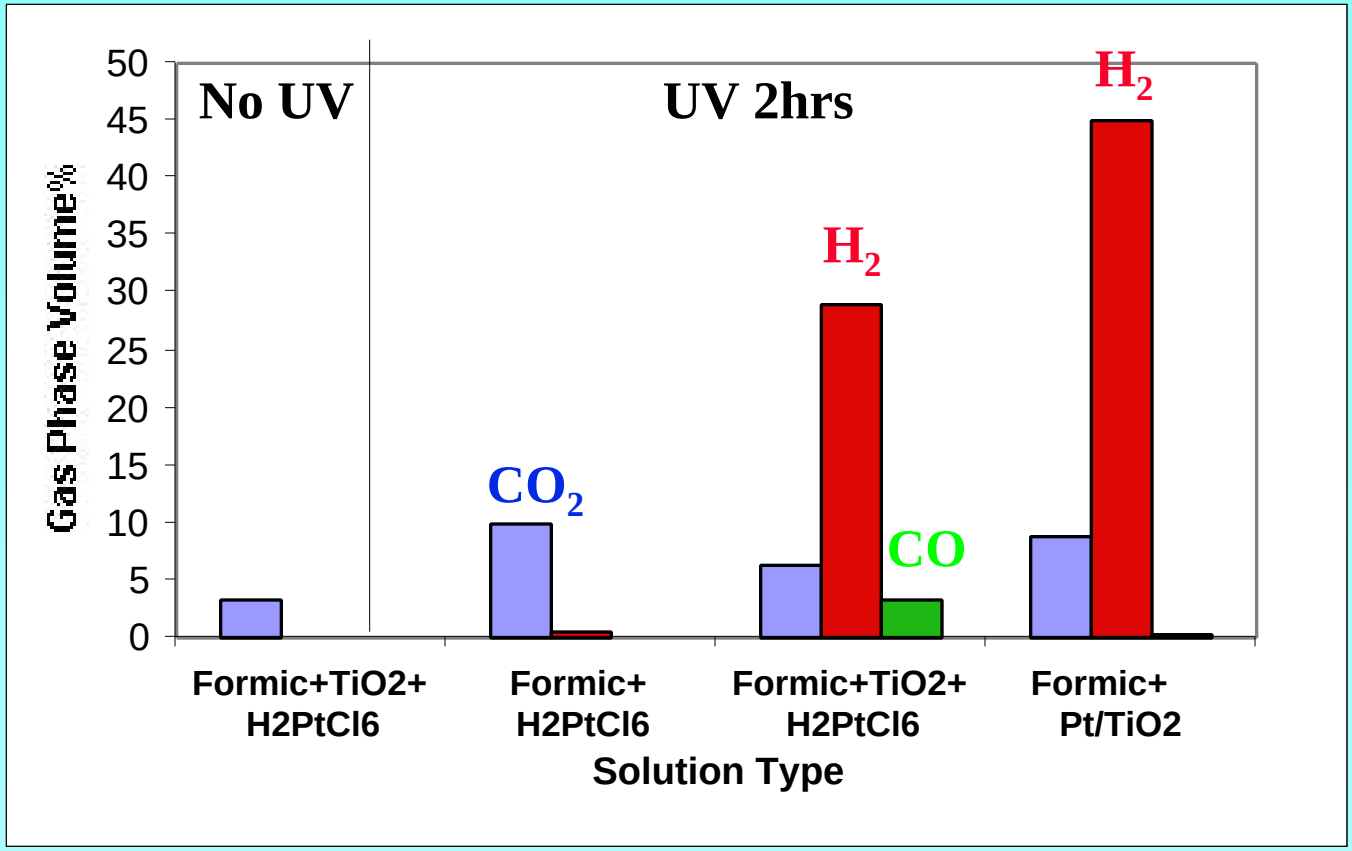
- H_2 Production in the presence of Pt/TiO_2 (N_2)

γ Radiocatalysis: H_2 Production



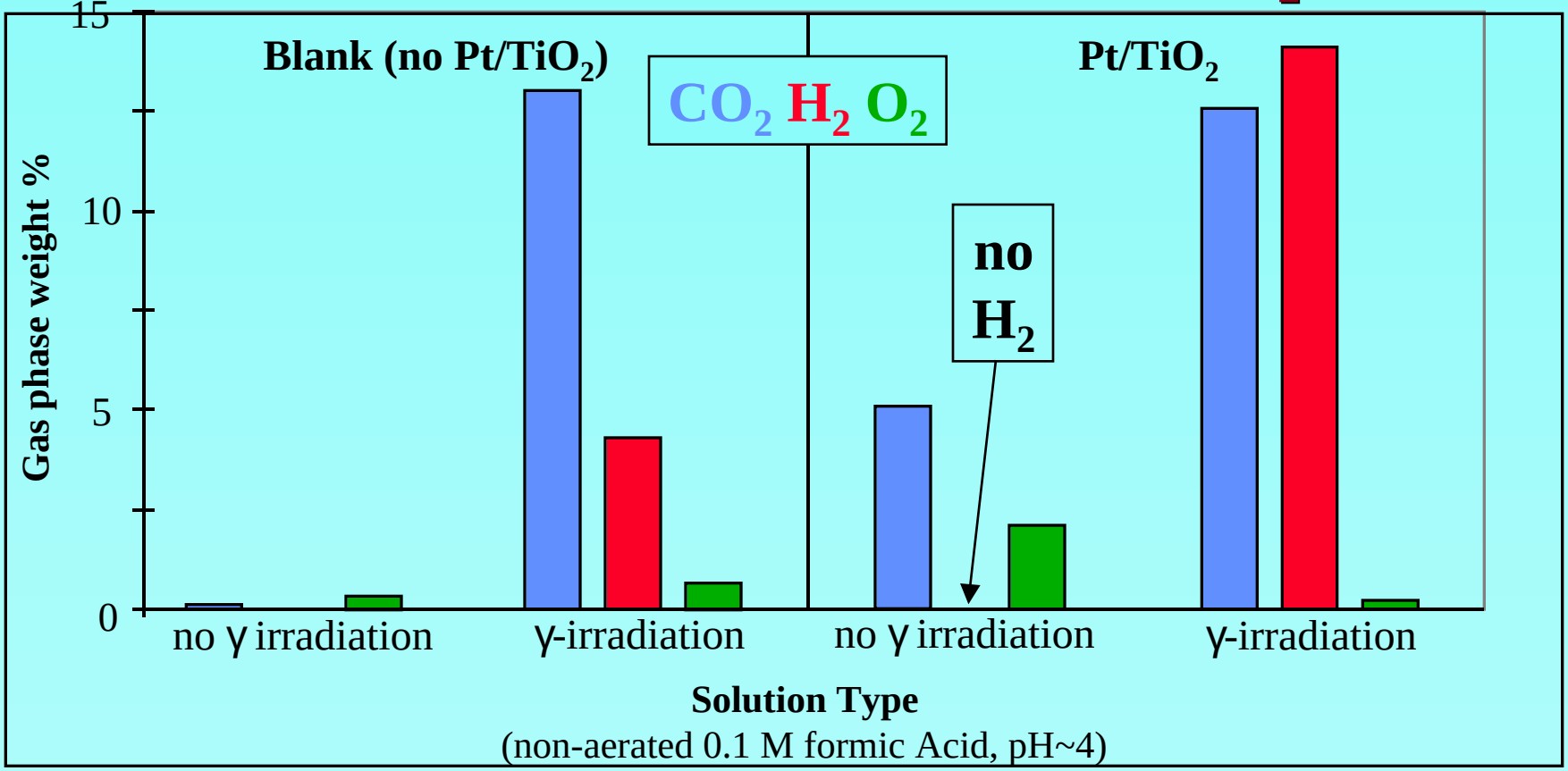
- H_2 Production in the presence of Pt/TiO_2 (O_2)

UV Photocatalysis: Pt^{4+} Reduction and H_2 Production



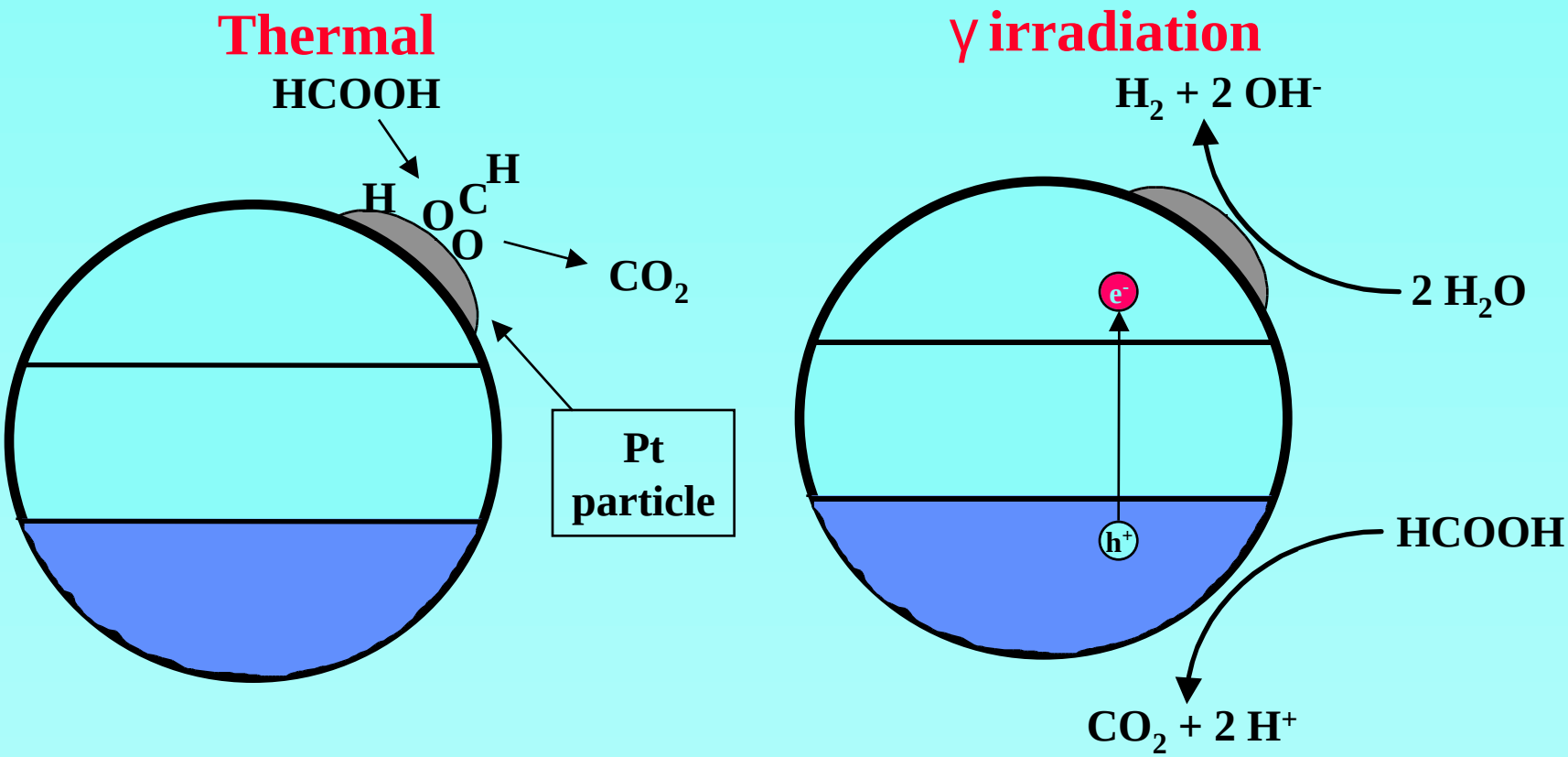
- Pt^{4+} is reduced to Pt^0 and HCOOH is oxidized to CO_2 on TiO_2 during UV irradiation

Gaseous Products During Radiocatalysis of Formic Acid in Colloidal Pt/TiO_2



- **Formic acid decomposes thermally and radiocatalytically by different mechanisms on colloidal Pt/TiO_2 particles**

Thermal and Radiocatalytic Decomposition of Formic Acid on Pt/TiO_2



- Although both mechanisms produce CO_2 from formic acid, e^-/h^+ processes explain H_2 production

Preliminary Conclusions

- **Zero-valent noble metals such as Pt can play a key role in the degradation of TPB. Nearly 100% of aqueously dissolved TPB (0.02M) was found to be destroyed within an hour in the presence of a Pt/TiO_2 catalyst *without* γ-irradiation.**
- **Benzene is a major product of TPB degradation in our studies.**
- **Aqueously dissolved metal cations (*e.g.*, Pt^{+4}) are reductively precipitated onto TiO_2 surfaces in the presence of UV photons or ionizing radiation.**
- **Reduction of Pt^{+4} and water cleavage into H_2 further indicate that the radiocatalysis mechanism is similar to that of UV photocatalysis.**