Radiocatalytic Degradation of Organic Contaminants in TiO_2 Suspensions

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Problems

- 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.**

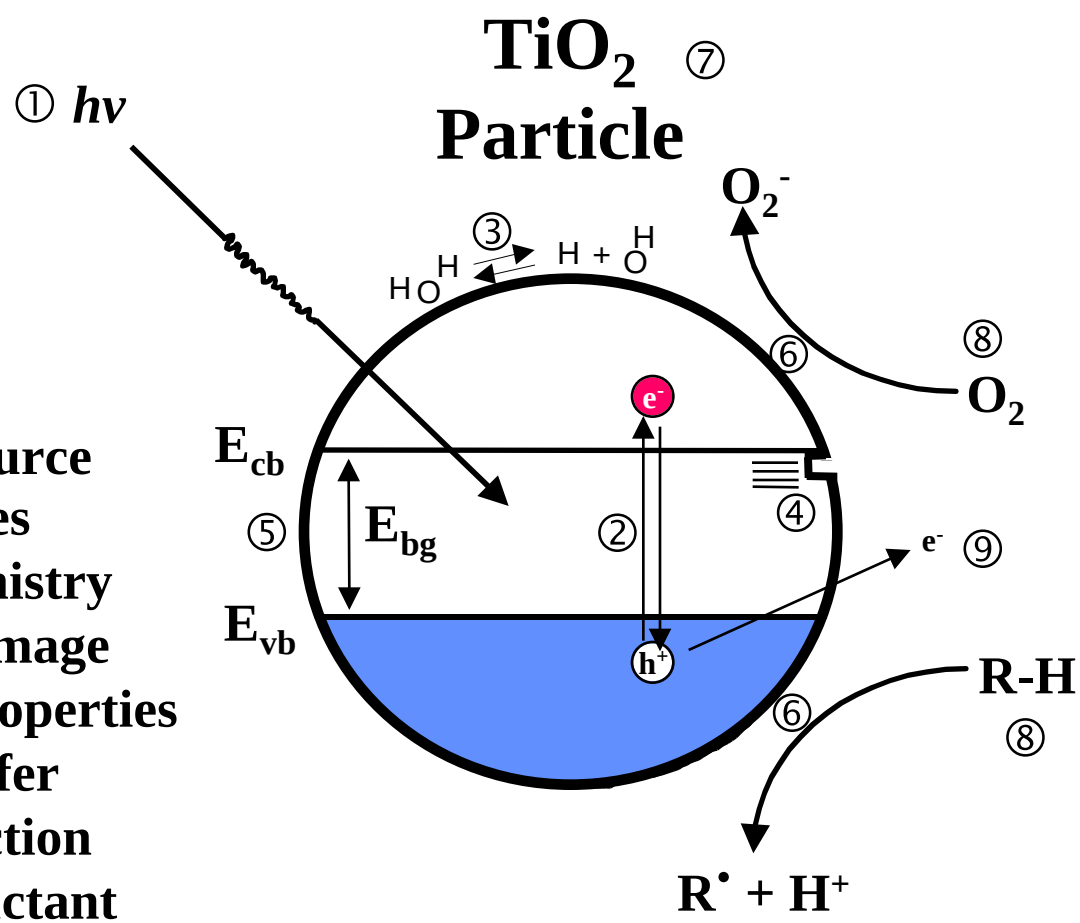
Objective

Investigate feasibility and mechanism of ionizing radiation induced radiocatalysis on stable, wide bandgap semiconductor catalysts.

This is a novel approach potentially useful for:

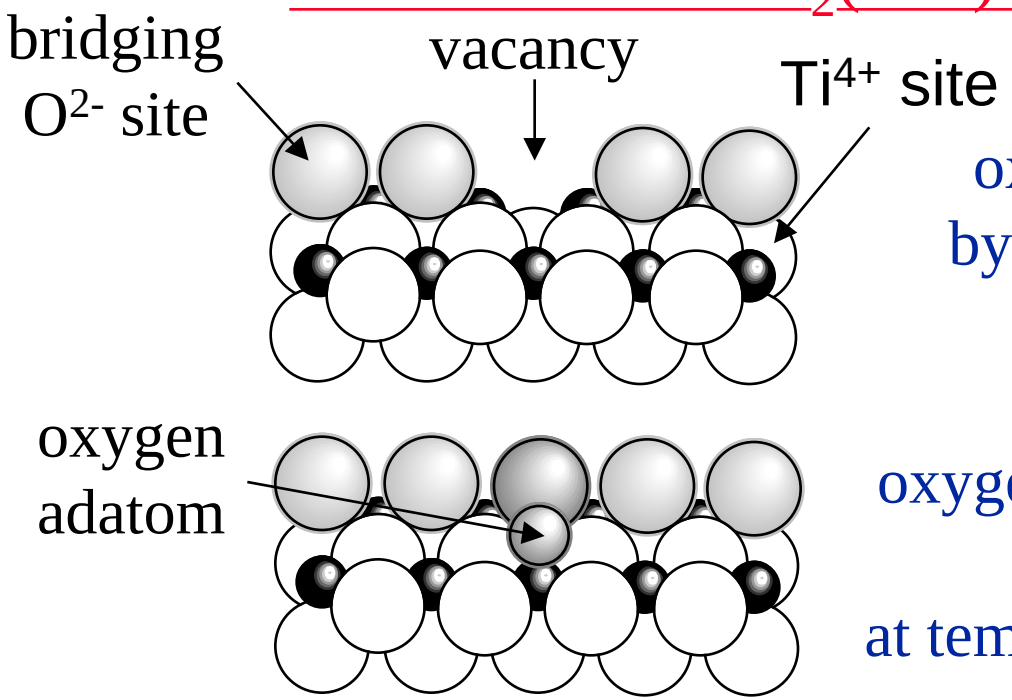
- **oxidation of organics**
- **reductive precipitation of metals and oxides**
- **understanding tank waste aging and radiation-induced damage in solids**

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

Formation of Oxygen Adatoms on Defective $TiO_2(110)$ Surfaces



oxygen vacancies form by particle bombardment or by annealing

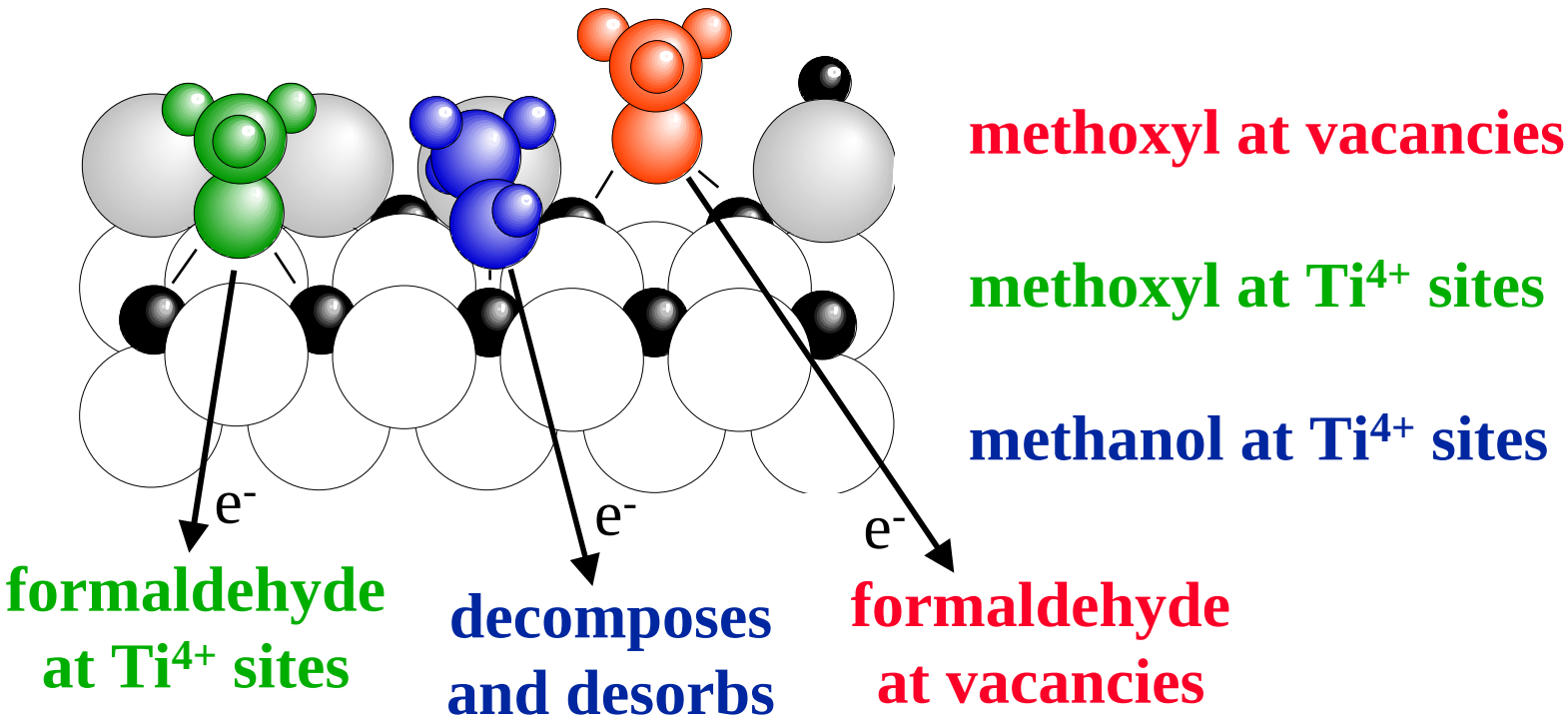
oxygen adatoms form when O_2 fills vacancies at temperatures below 600 K

Preliminary results suggest these adatoms:

- **are thermally stable**
- **break C-H, O-H and N-H bonds**
- **oxidize N_2 to NO and/or N_2O**

(Epling, et al., Surf. Sci., in press.)

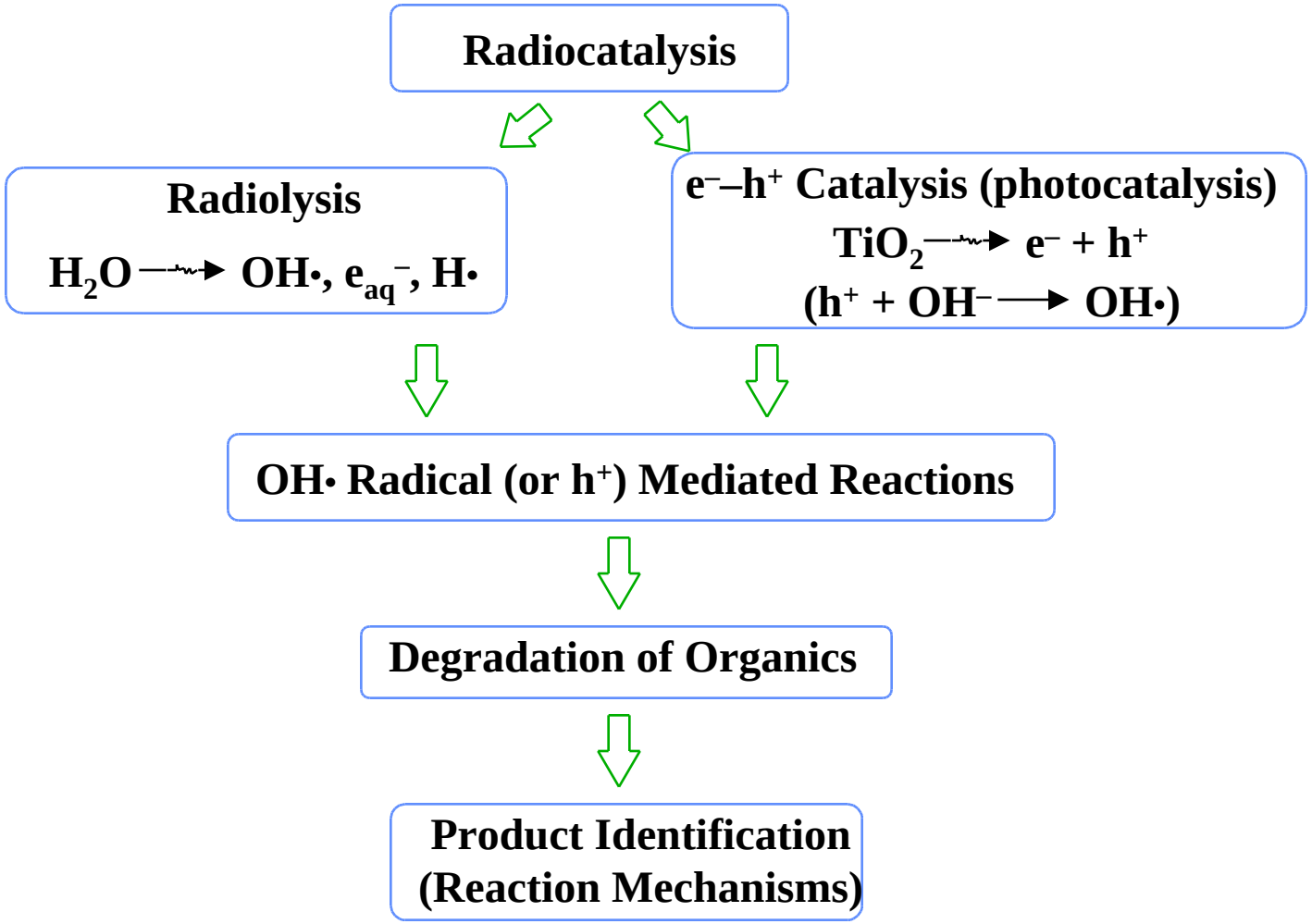
Activation of Methanol Species on TiO_2(110) by 100 eV Electron Irradiation



- **Cross-sections are ≥ gas phase values; TiO_2 does not quench e^--induced excited states**

(Henderson, et al., Surf. Sci., in press.)

Radiocatalysis



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

Approach

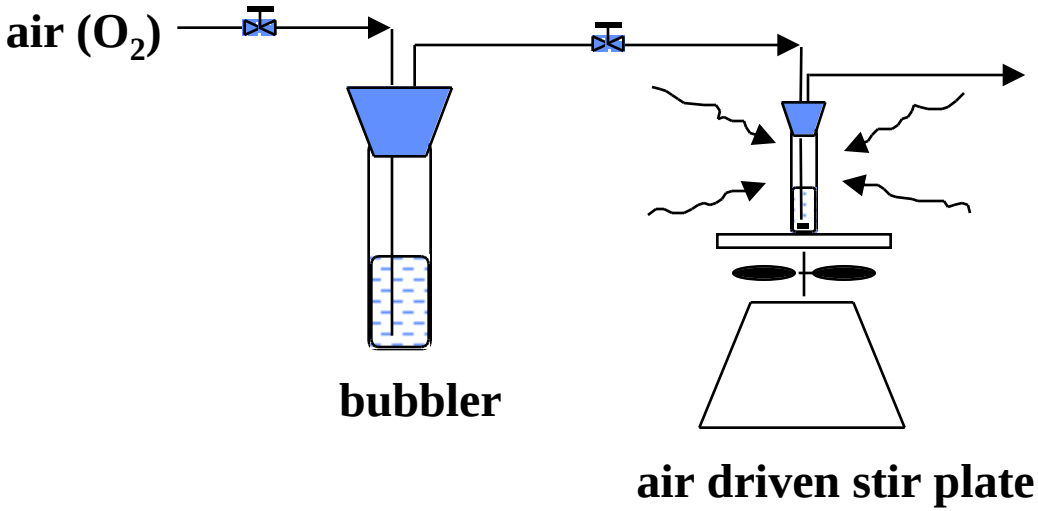
- **Choose EDTA as a model organic chemical system.**
- **Examine EDTA degradation in TiO_2 suspension under γ irradiation. Explore:**
  - **— O_2 effect**
  - **— product formation**
  - **— pH dependence**
  - **— Sr^{2+} chelation effect**
  - **— comparison with UV photocatalysis**

- **Use HPLC, IC, GC/MS techniques to determine initial compound and final products.**

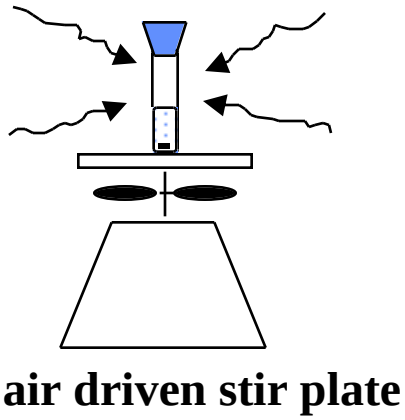
Experimental Conditions

- **Substrate:** 0.02M aqueous EDTA solution
- **Catalysts:** 1) 0.01 ~ 0.1 g/ml TiO_2 (Degussa P-25)
  2) 0.01 ~ 0.1 g/ml 1%Pd/TiO_2
- **γ Irradiation:** 1~ 7 MRad from ^{60}Co source
  (solutions continuously stirred to suspend TiO_2)
- **Analysis:** 1) HPLC
  2) IC
  3)GC/MS

Experimental Setup

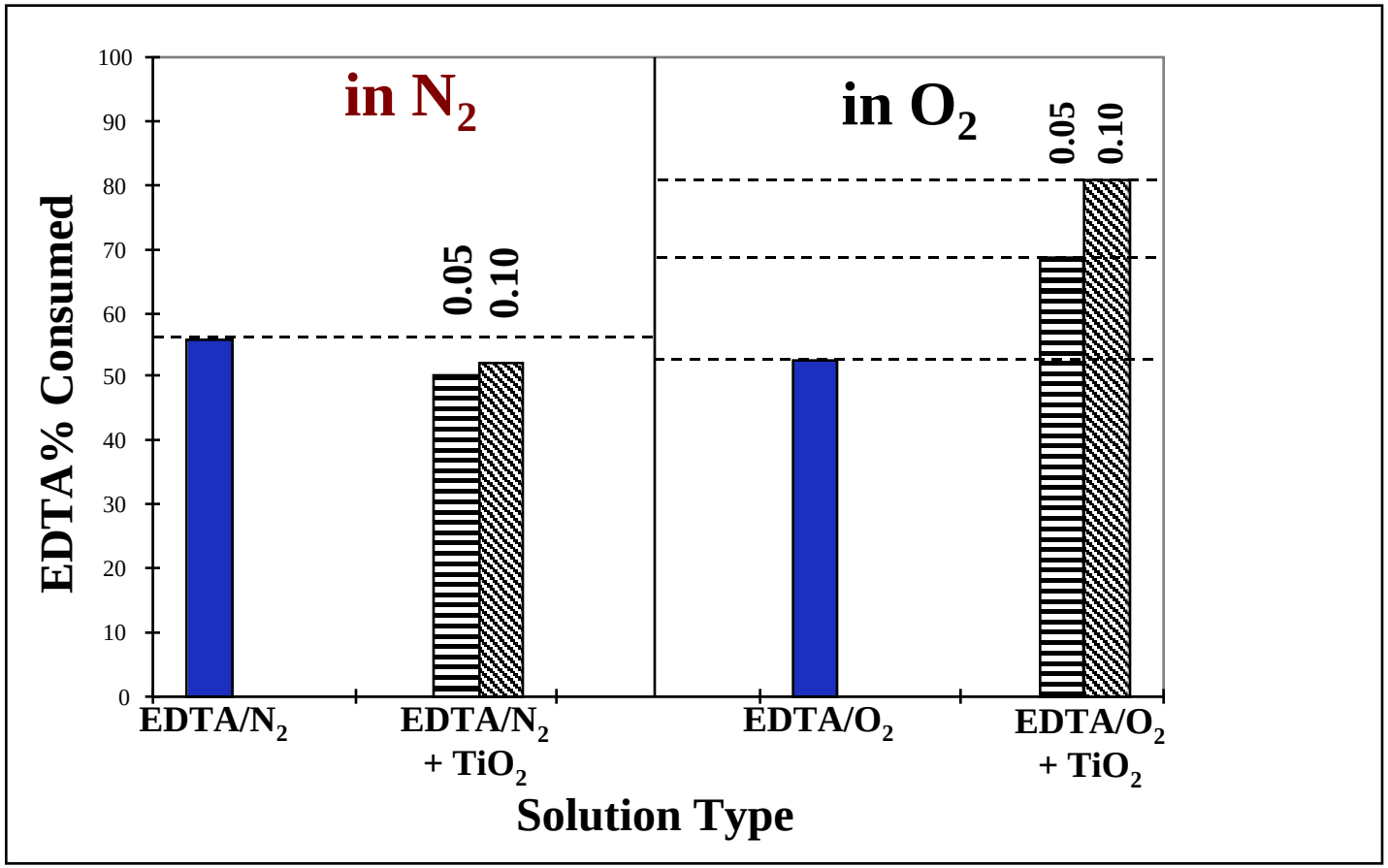


(a) gas flowing system



(b) static gas system

Effect of O_2 and TiO_2 on degradation of EDTA

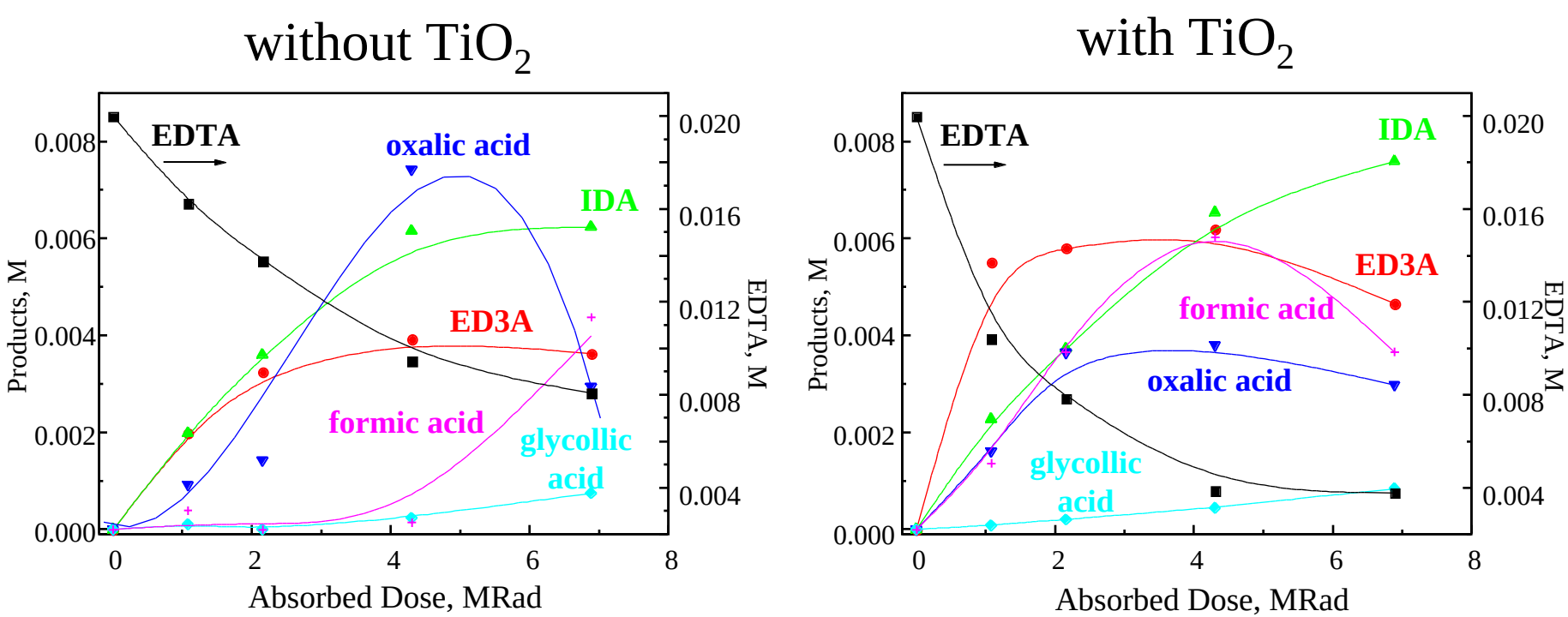


- **O_2 plays a key role (electron scavenger) on the degradation of EDTA in TiO_2 suspension.**
- **30% more EDTA degradation in the presence of 0.1 g/ml TiO_2.**

Radiocatalysis works !

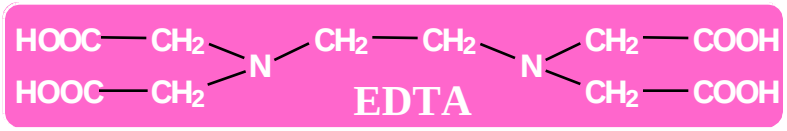
(Su, et al., J. Adv. Oxid. Technol. 3 (1998) 63)

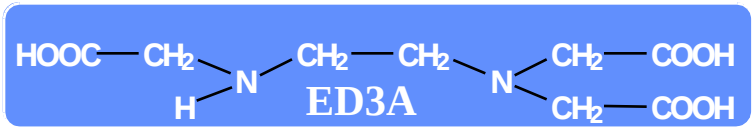
Concentrations of EDTA and Radiolytic Products as a Function of Absorbed Dose

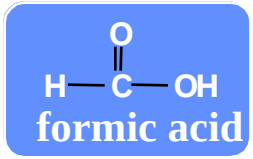


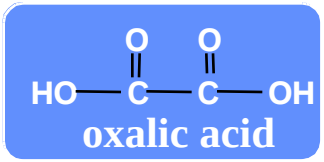
- **TiO_2 significantly promotes the degradation of EDTA.**
- **Identified products: ED3A, IDA, glycolic, oxalic, and formic acids.**

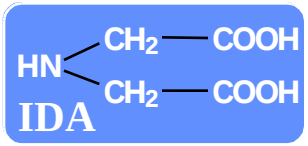
Abbreviations

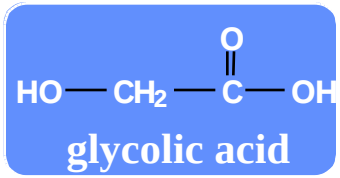




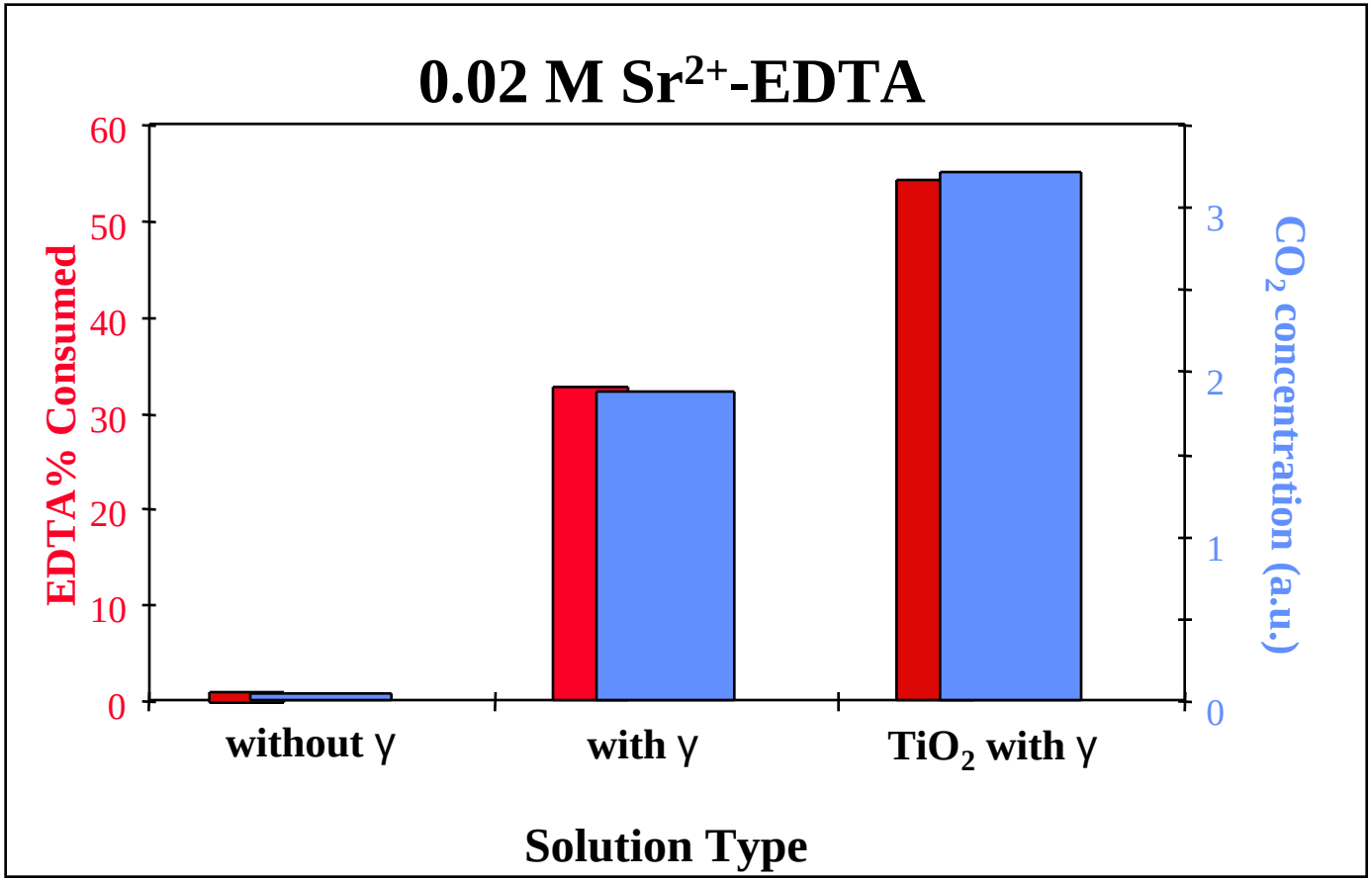






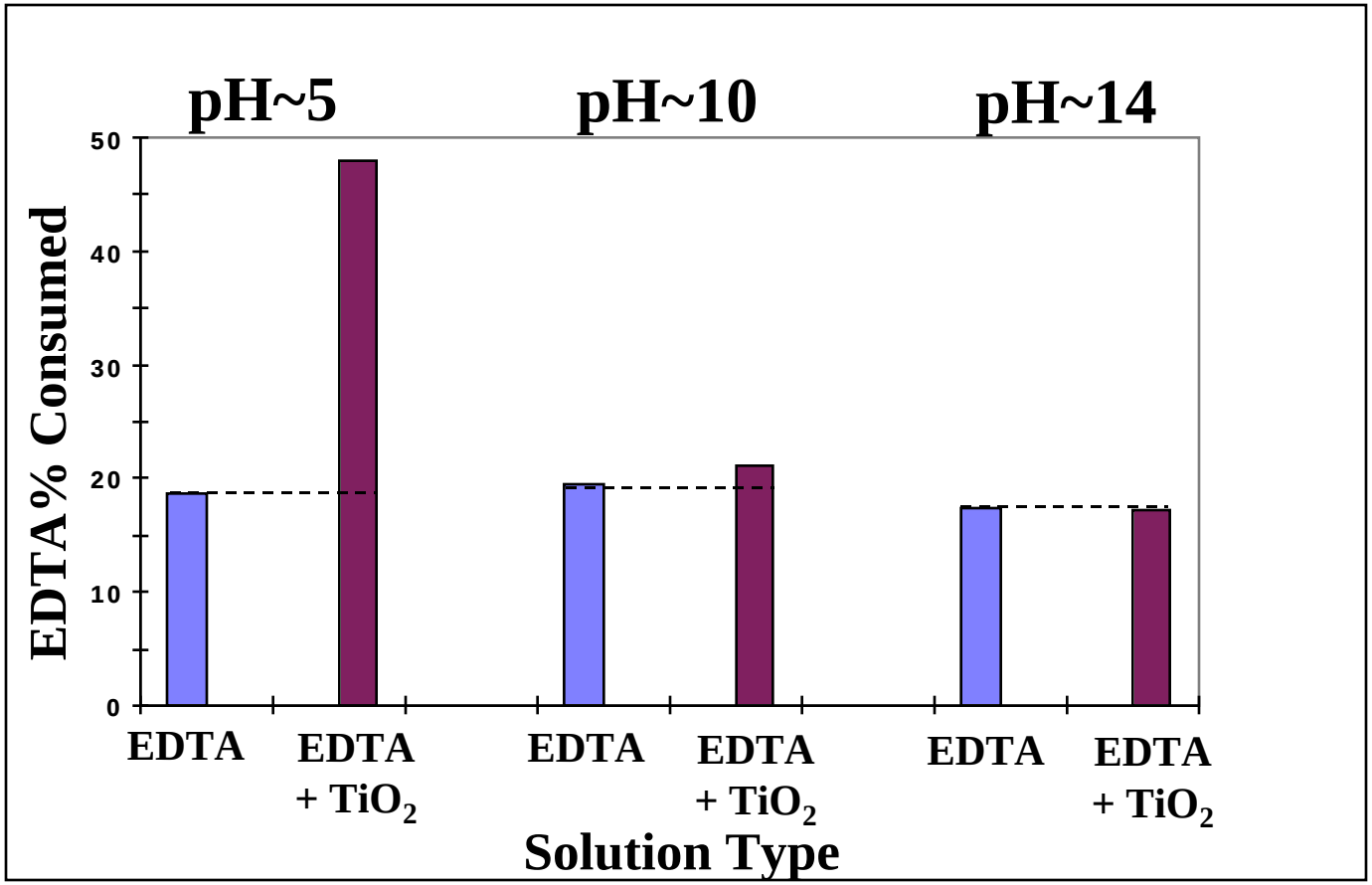


CO_2 Production from EDTA Degradation



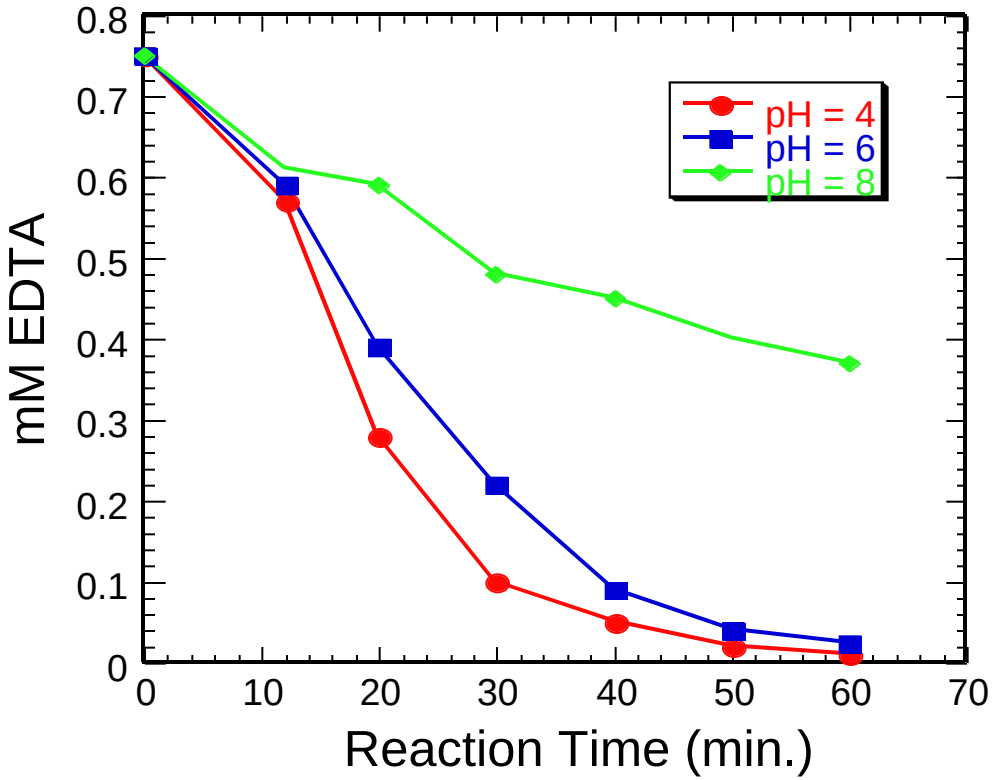
- CO_2 formation tracks EDTA degradation.

pH Dependence of EDTA Degradation



- No TiO_2 promotion of EDTA degradation at high pH.

pH Dependence of EDTA Degradation for UV Photocatalysis

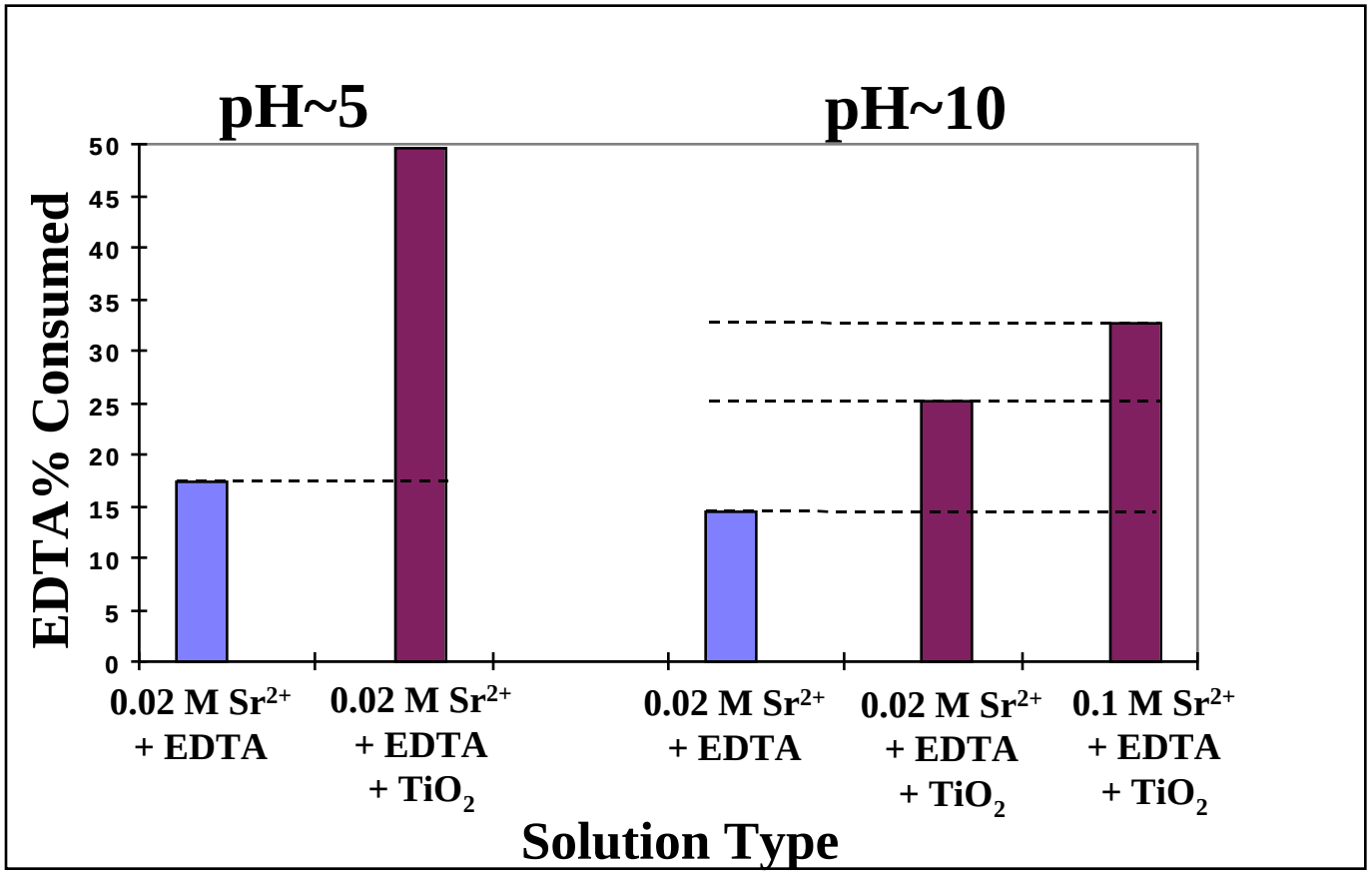


- **Reaction rates decrease dramatically at pH's above the isoelectric point of TiO_2.**

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

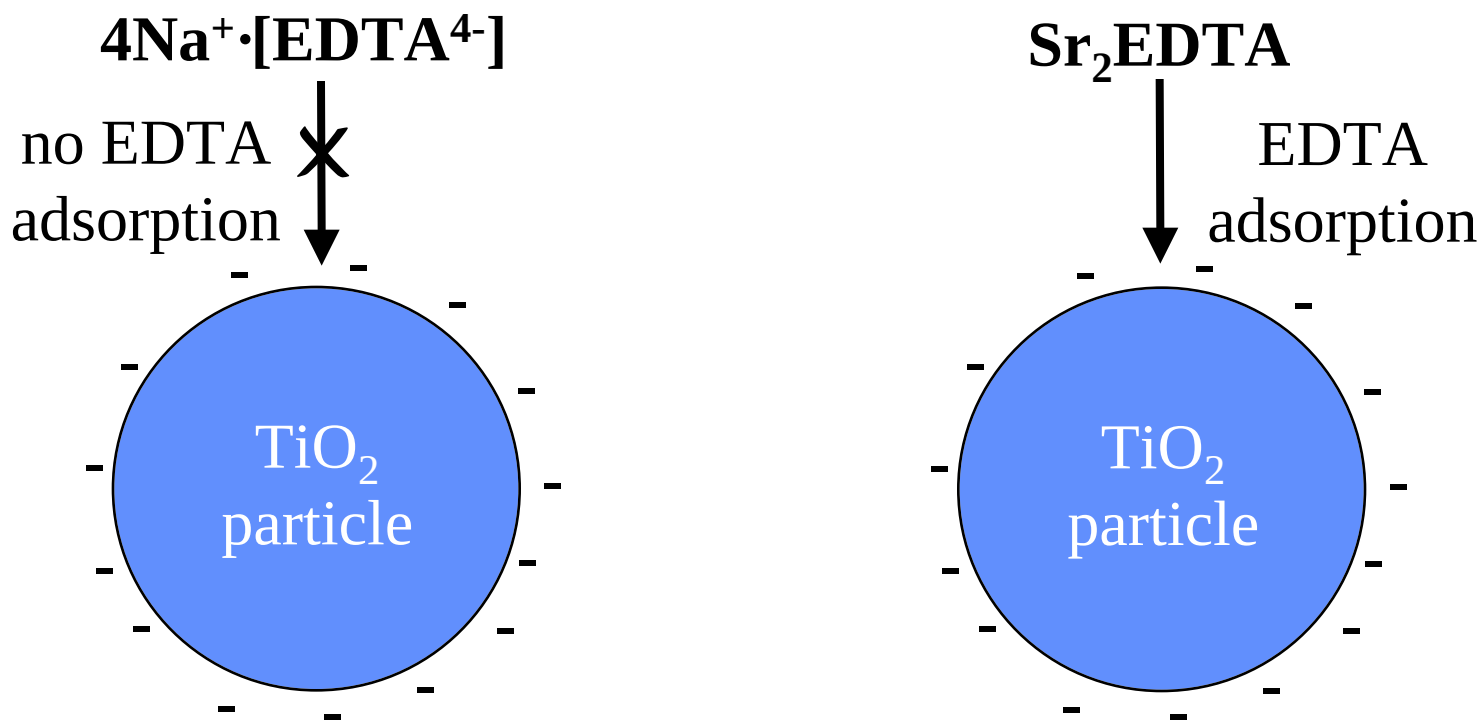
- **pH dependence in radiocatalysis matches that observed in UV photocatalysis**

pH Dependence of Sr(2+)-EDTA Degradation



- 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.**

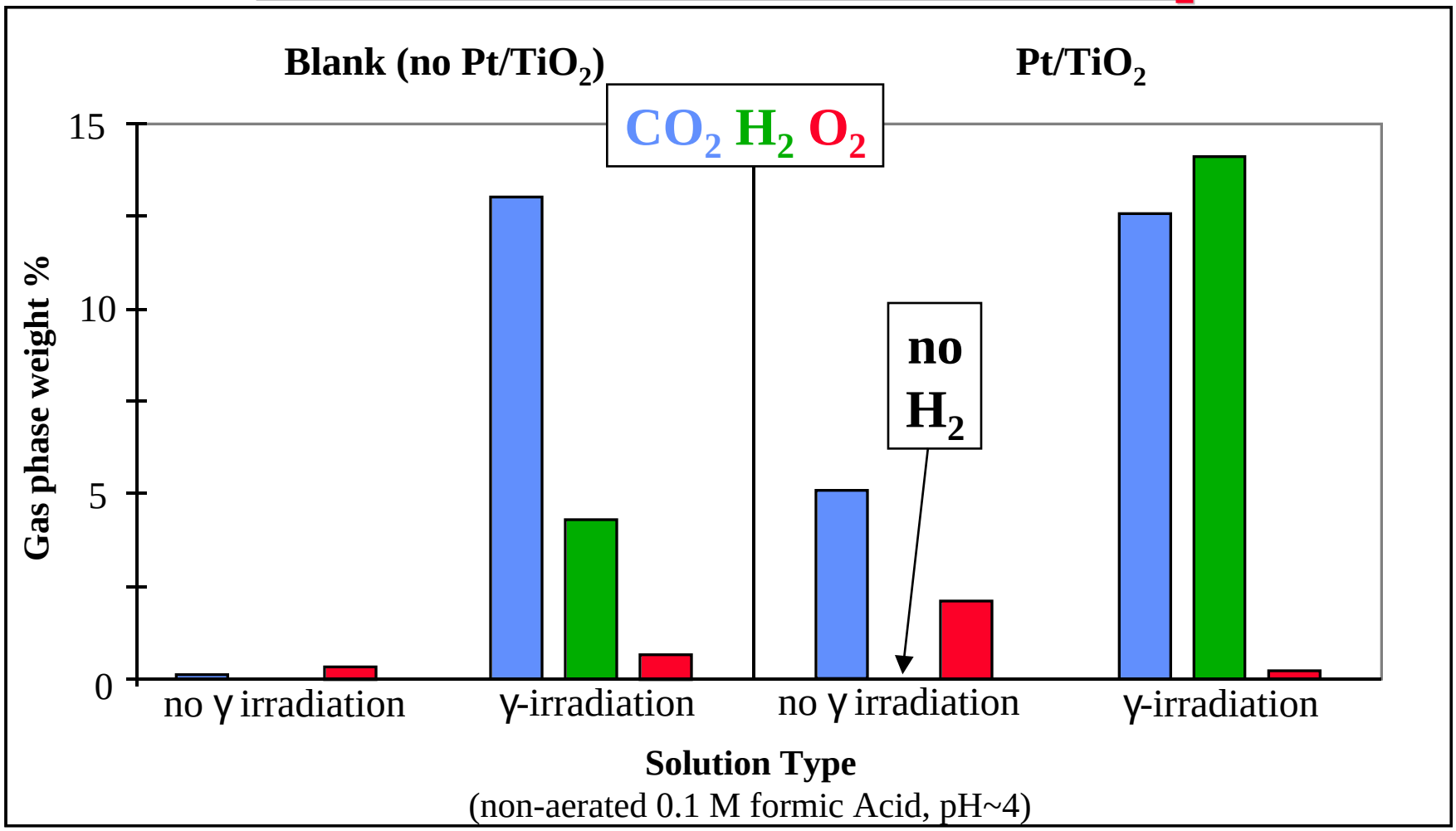
Summary

- **The study reported here represents, to our knowledge, the first use of a continuous 'radiocatalytic' process to degrade organics with a TiO_2 catalyst.**
- **TiO_2 can increase the destruction of EDTA up to 40-50% compared to radiolysis.**
- **Similarities with UV photocatalysis have been observed suggesting that e^-/h^+ processes are important.**

Future Directions

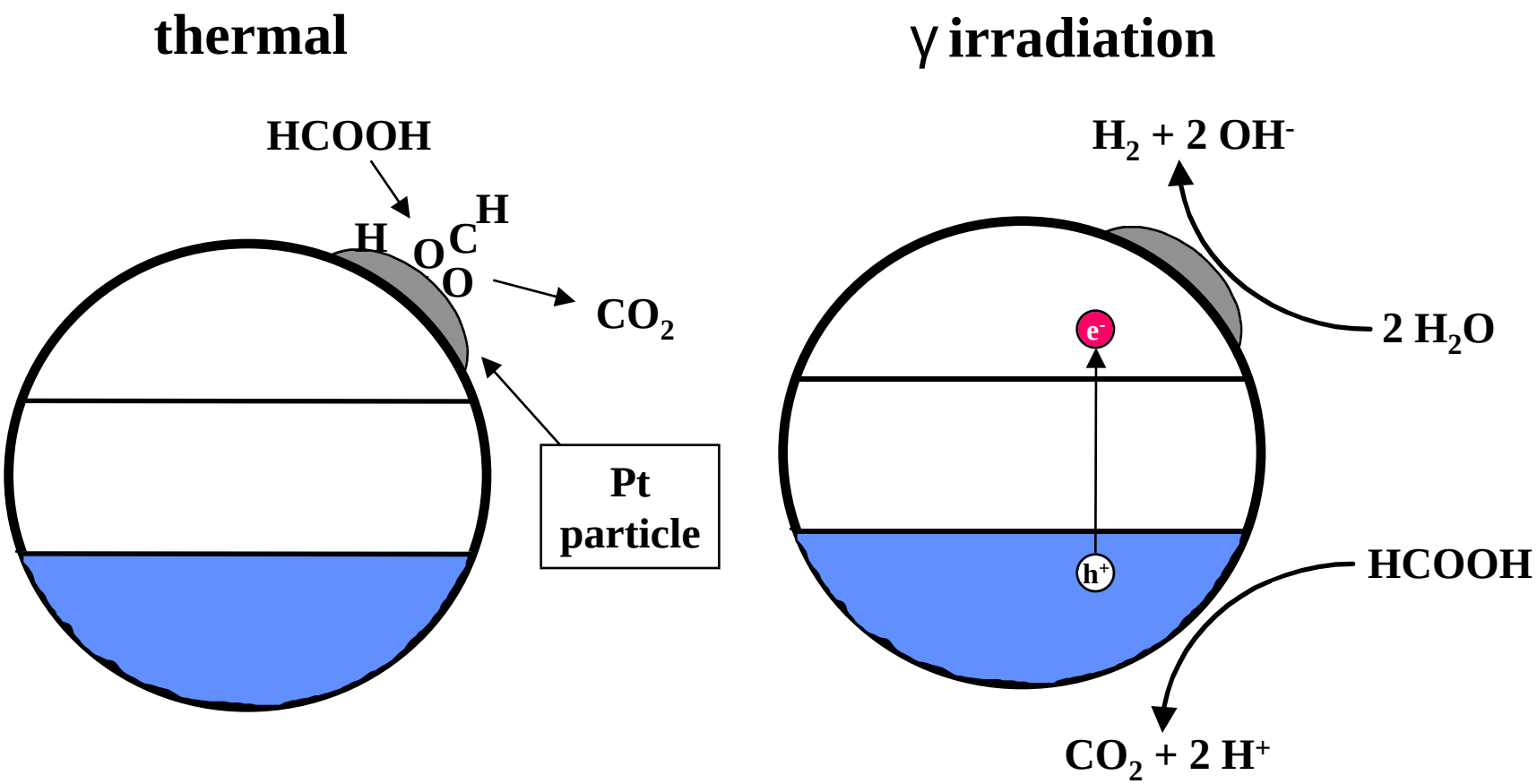
- **Use of simpler organic substrates for studies of the reaction mechanism:**
  - further validate the e^-/h^+ mechanism
  - explore other mechanistic possibilities
  - utilize ultrahigh vacuum (UHV) methods
- **Initial studies of structure-sensitivity for UV photocatalysis.**
- **Scoping studies of ZrO_2 'radiocatalytic' chemistry - focus on reductive metal deposition.**
- **Preparation of model ZrO_2 surfaces for studies in UHV.**

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



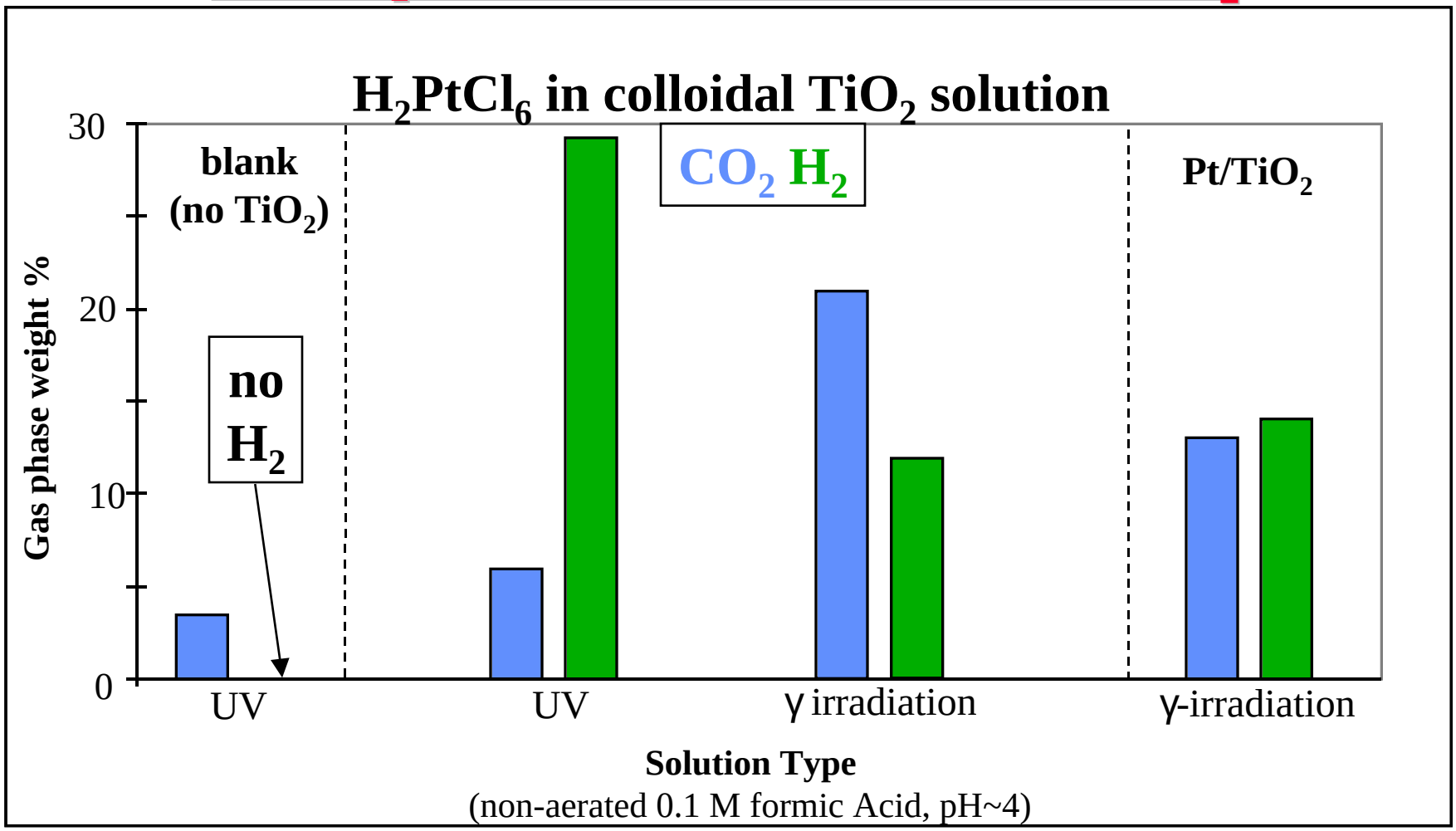
- **Formic acid decomposes thermally and radiocatalytically by different mechanisms on colloidal Pt/TiO_2 particles**

Thermal and Radiocatalytic Decomposition of Formic Acid on Pt/TiO2



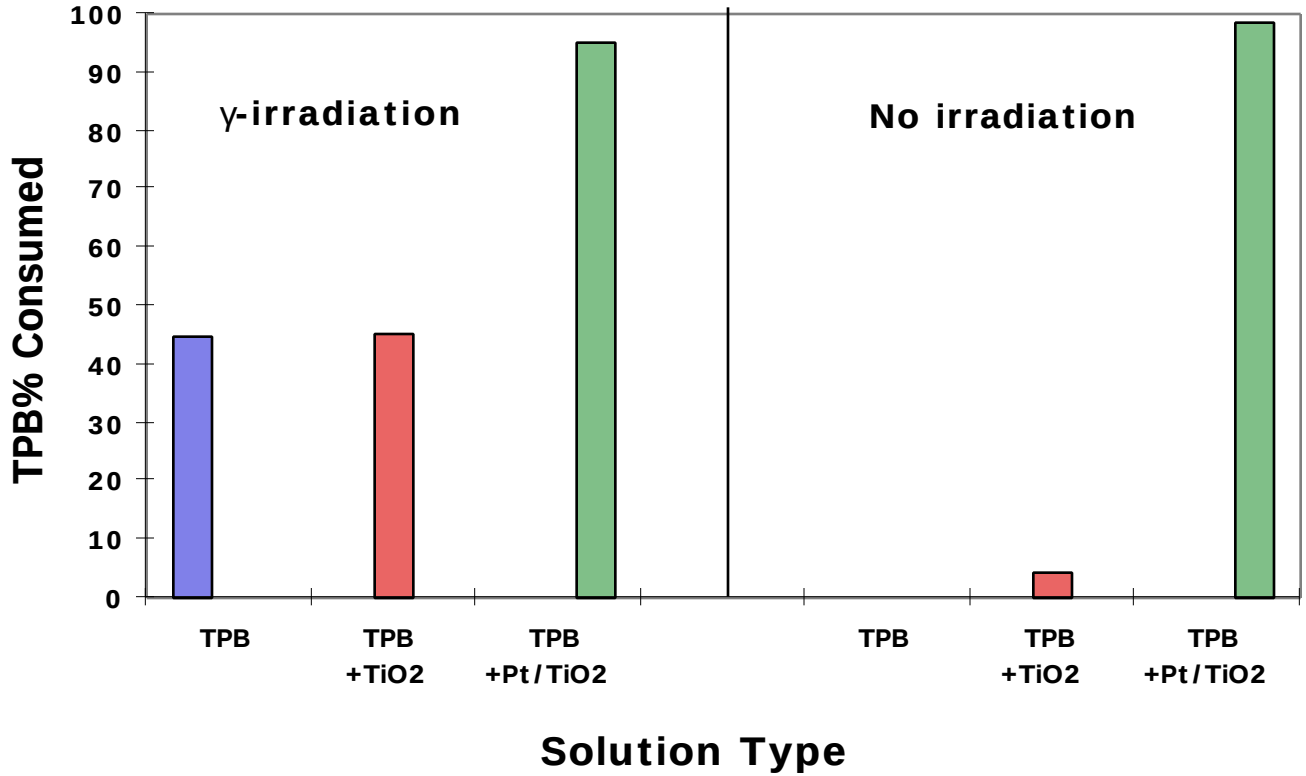
- Although both mechanisms produce CO_2 from formic acid, e-/h+ processes explain H_2 production

Reduction of Pt(4+) During Radiocatalytic Decomposition of Formic Acid on TiO_2



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

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



- 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.