Catalytic materials for plasma-based VOC removal

David Cameron, Tatyana Ivanova, Marja-Leena Kääriäinen

Advanced Surface Technology Research Laboratory (ASTRaL)

Lappeenranta University of Technology

Finland

plasma for environment protection

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Outline

- Why use plasma + catalyst?
- Reactor configuration
- Technology of coating with catalyst
- Some performance results
- Summary

Why use plasma + catalyst?

PlasTEP
plasma for environment protection

In the plasma system with no catalyst;

- Air + hazardous impurities passed through a plasma discharge
- Bombardment of molecules by electrons and ions.
- Formation of ozone, atomic oxygen, hydroxyl groups, excited molecules and atoms
- Oxidation of VOCs to CO_2 and H_2O

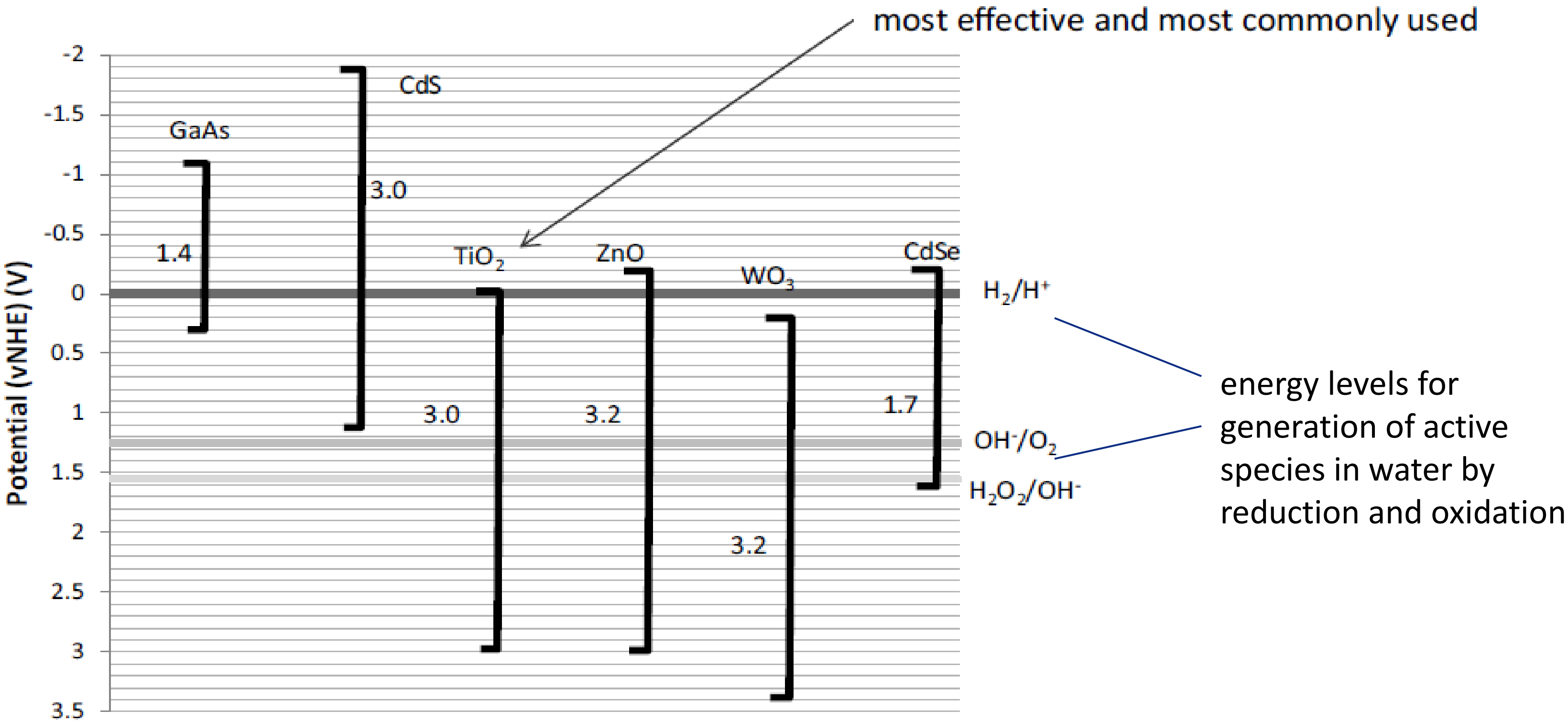
Characteristics

- Not always complete decomposition of VOCs to CO_2 and H_2O at acceptable discharge energies especially if VOC levels are high
- Residual ozone from outlet which must be removed

  —needs a removal stage after the plasma stage
- Can incorporate a catalyst in the system to improve decomposition and remove hazardous byproducts
- Standard catalysts need a high temperature
- Use an activated catalyst

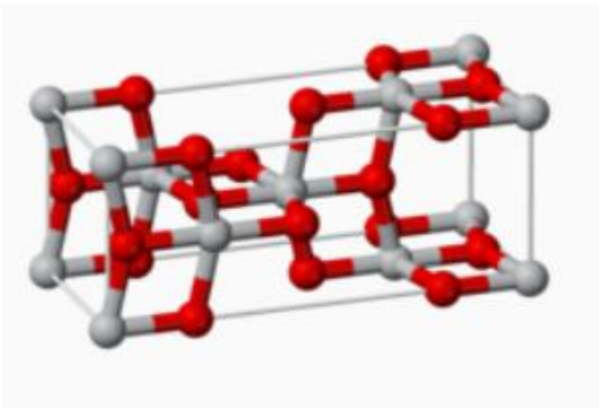
Photocatalysts

- Semiconductors are effective photocatalysts
- Need photoactivation by appropriate wavelengths
- Use plasma radiation to activate catalyst – don't need high temperatures to activate

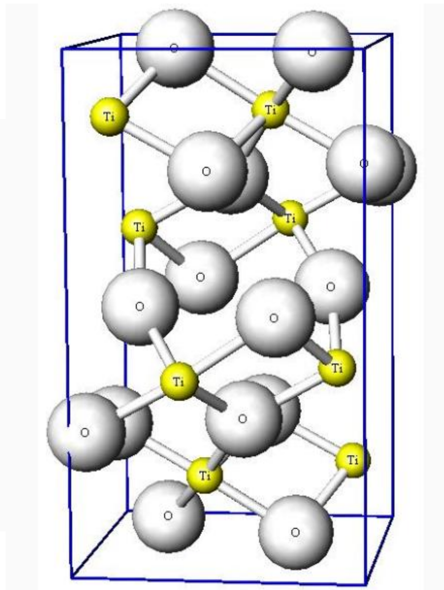


Titanium dioxide

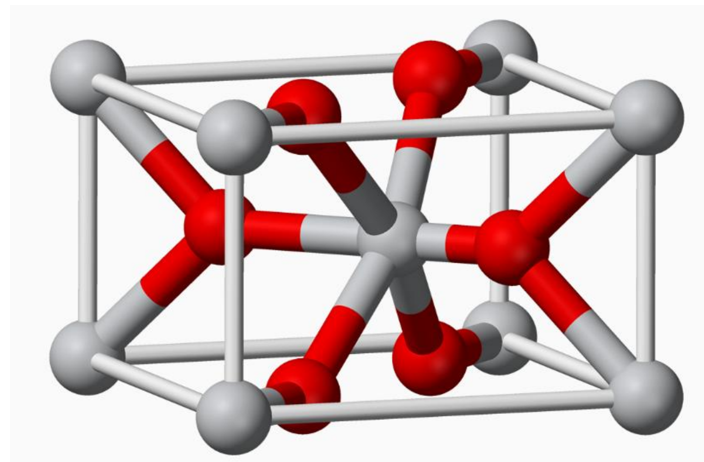
3 crystal phases



Anatase
energy gap 3.2 eV
stable at low temperature

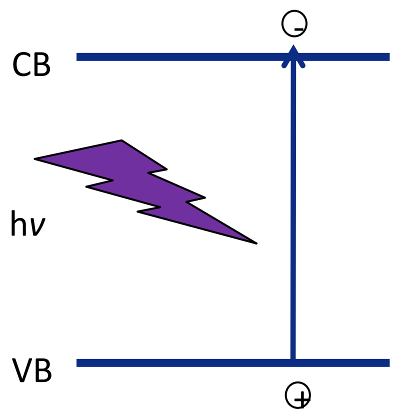


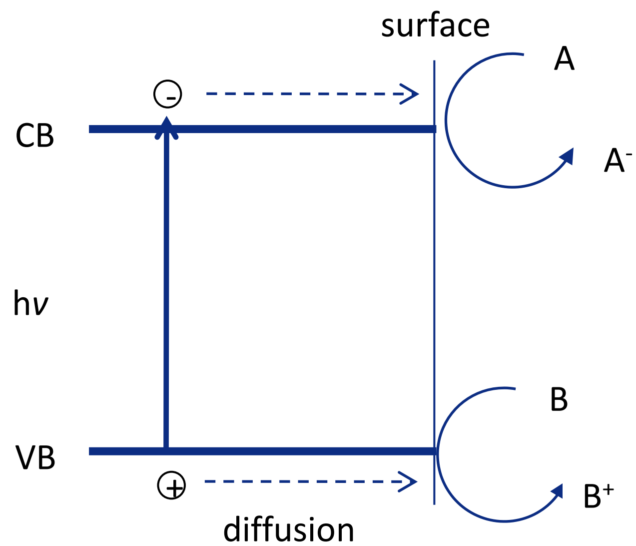
Brookite
energy gap 3.3 eV



Rutile
energy gap 3.0 eV
stable at higher temperature

Mechanism of photocatalysis



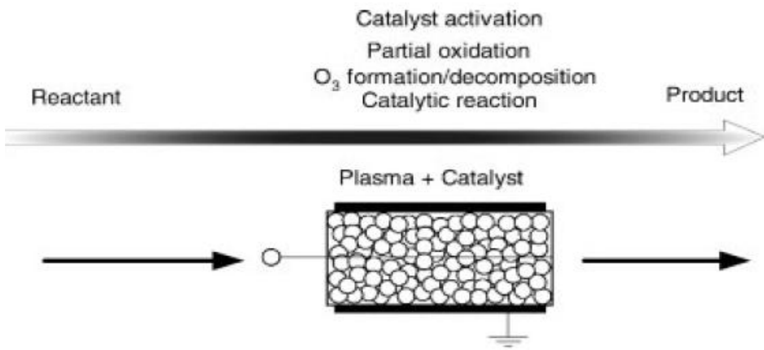


Electrons and holes generated inside the catalyst must get to the surface so that they can cause a reaction.

Electrons and holes must diffuse to the surface in order to act on adsorbed species

Needs light with energy greater than bandgap to activate the catalyst – fpr TiO_2 use UV light from the plasma

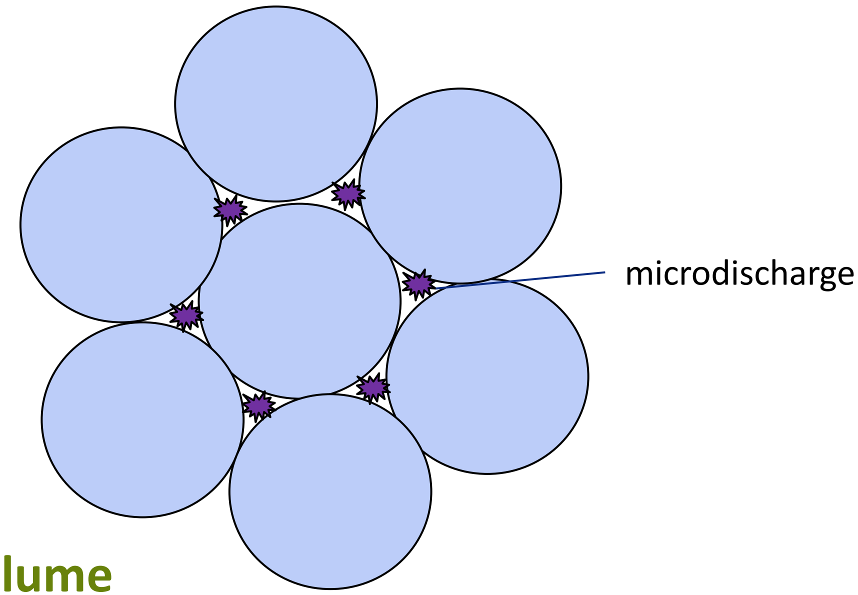
Single-Stage Plasma Catalysis



- Combination of gas phase and surface reactions
- Reactions take place simultaneously
- Complicated reactions
- Maximises interaction of catalyst with plasma
- Can utilise short-lived plasma species to interact with the catalyst

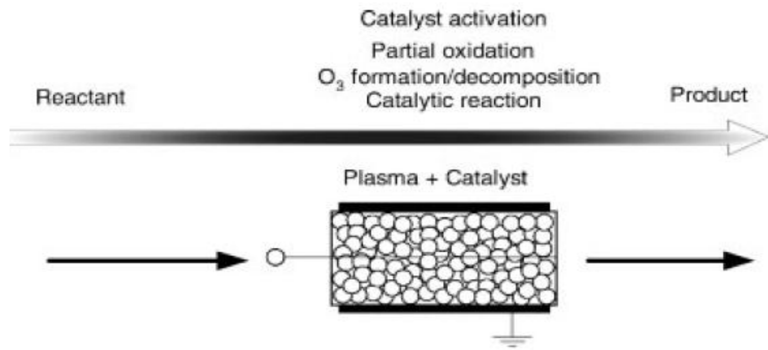
Discharge enhancement

- With single stage plasma, microdischarges can be generated inside pores or gaps between particles



- More discharge energy per unit volume
- Higher mean energy density
- Electrical properties of particles are important

Packed bed structure



To maximise the surface area of the catalyst, it can be in

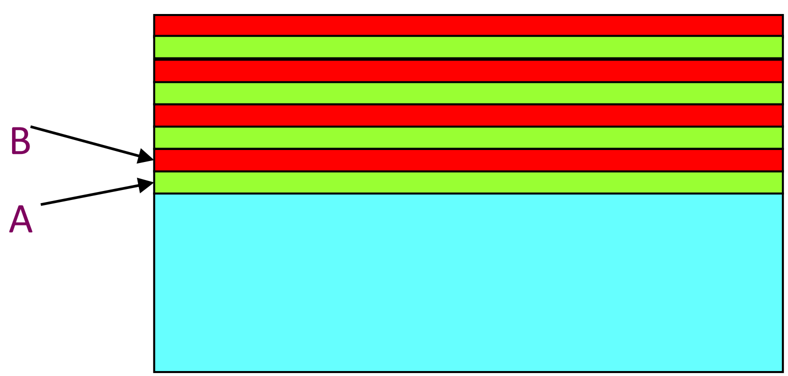
- pellet form, homogeneous or coated
- coated fibres

Our solution is to use porous materials with small pore size to maximise surface area

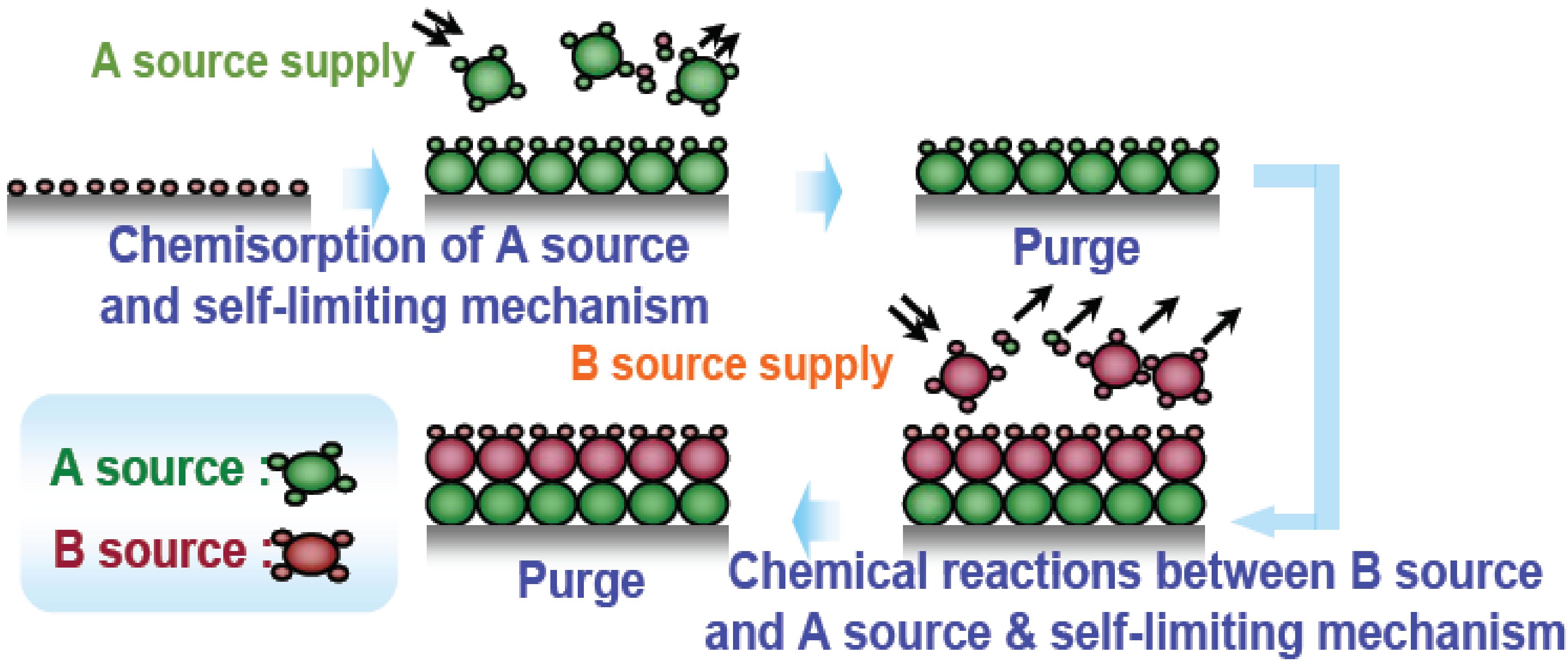
- how to coat internal surfaces of the pores?

Atomic Layer Deposition (ALD)

- Materials are built up one atomic layer at a time.
- For example, a compound AB is built up of alternate layers of A and B one atomic layer thick at a time.
- Extremely conformal coating
- Can coat inside porous structures – if pores are bigger than precursor molecules



ALD process cycle



Repeat as many times as required

Characteristics of ALD

- Chemical vapour deposition process
- Film thickness sub-nm to several hundred nm
- Extreme control over deposition – thickness controlled ’digitally’,
  - depends on number of deposition cycles
- Complete conformality, even on complex shapes, within pores and on nanoparticles
- Can change the composition from layer to layer

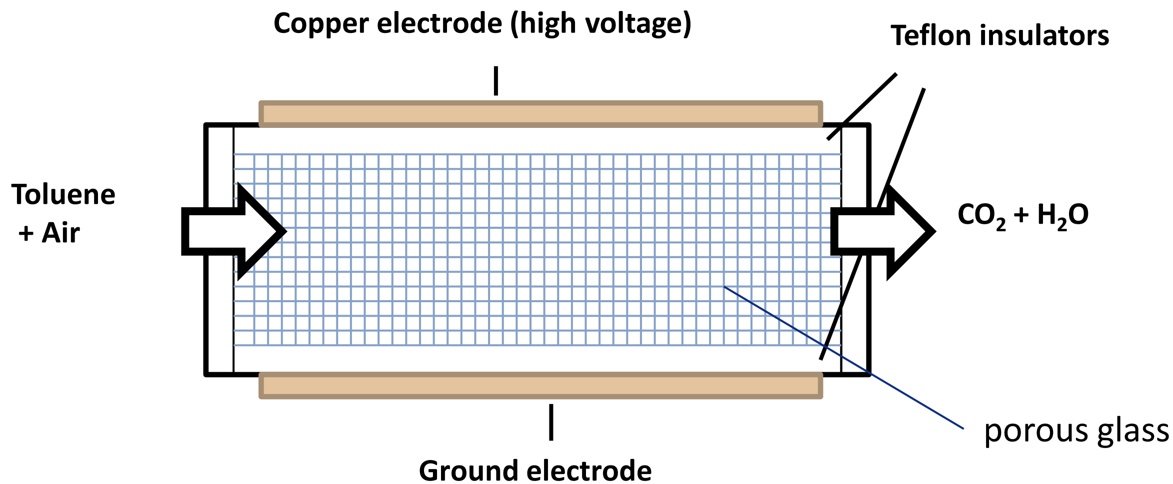
ALD process for TiO_2

- **Precursors $TiCl_4$ and H_2O**
  - **both have a high enough vapour pressure at room temperature**
- **Reaction temperature 300°C**
  - **gives mainly anatase material**

Beneq TFS 500 reactor

Plasma reactor

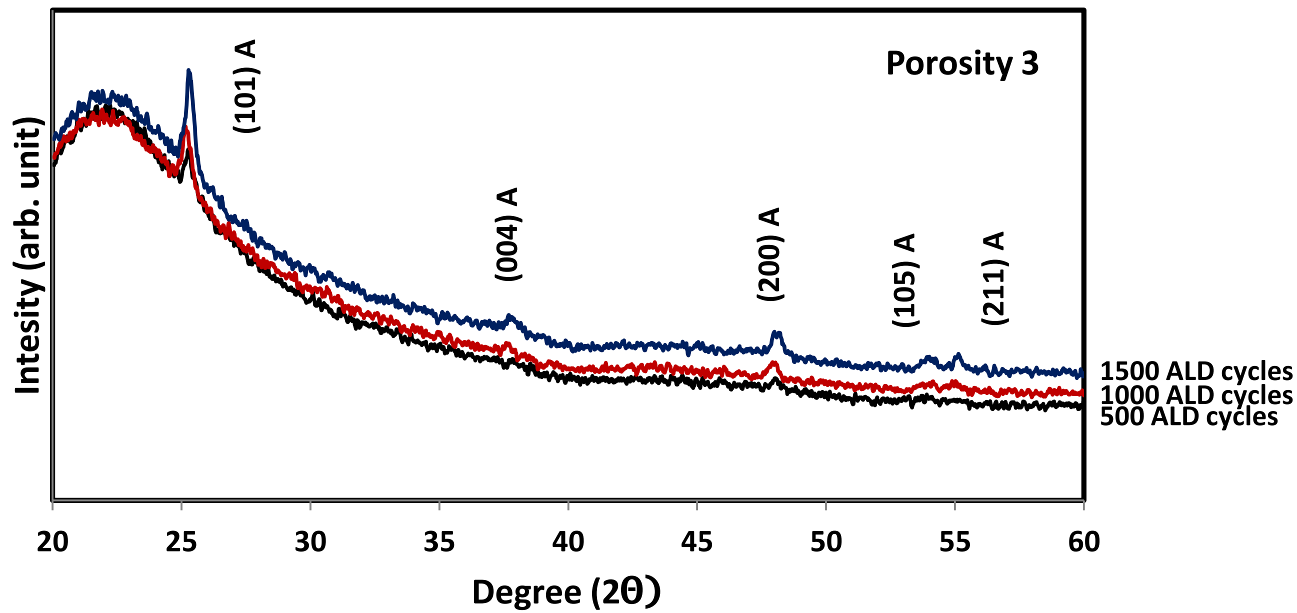
- Dielectric barrier discharge reactor



- Single stage reactor – plasma and catalyst in the same chamber
- Discharge gap with porous glass filling
- Pores coated by ALD

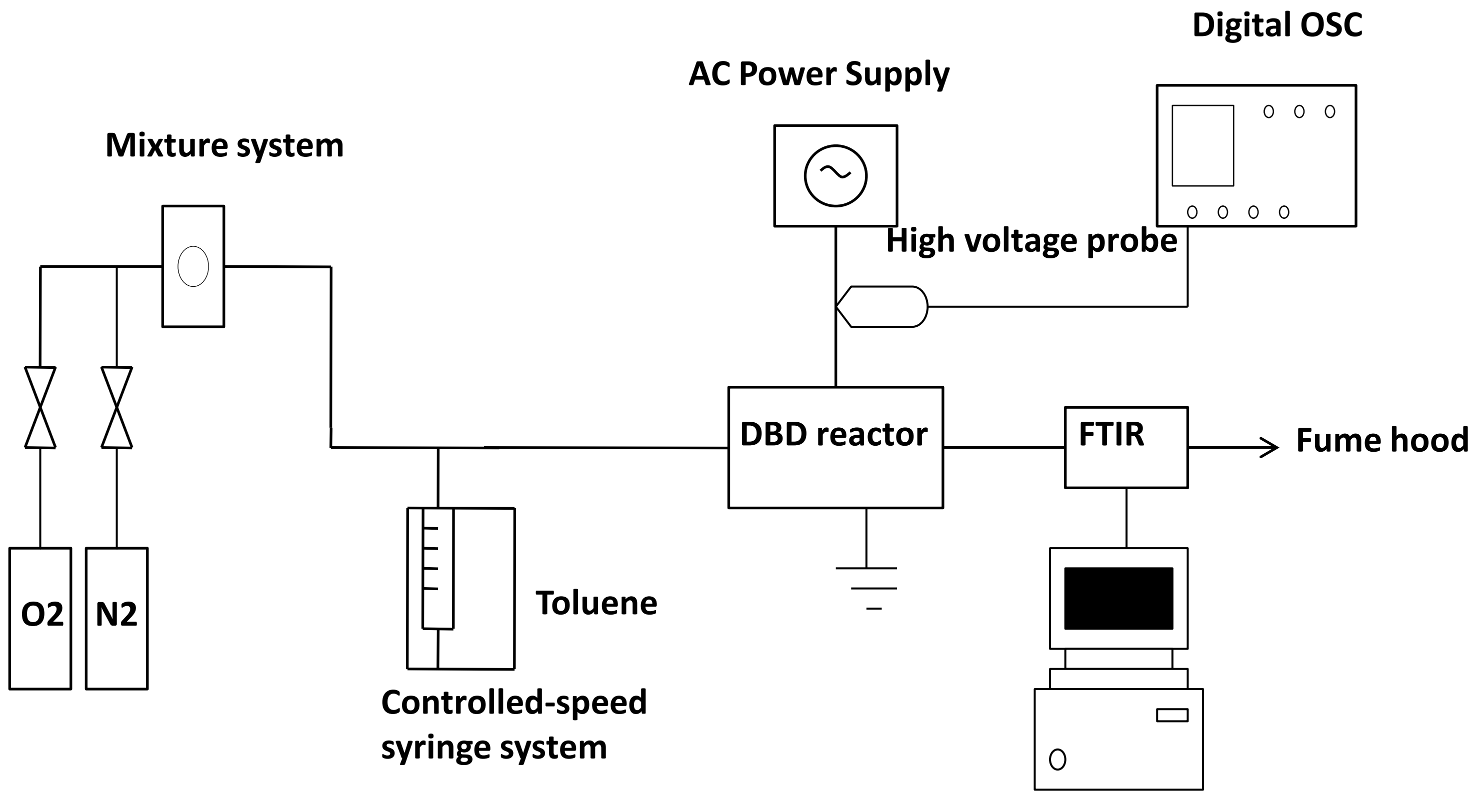
Film structure

XRD analysis



anatase structure

Experimental set-up for measuring toluene degradation



Efficiency of removal of VOCs

- **Carbon balance**

$$\text{Carbon balance } (\%) = \frac{[CO_2]+[CO]}{n([VOC]_0 - [VOC])} \times 100$$

n = no. of C atoms in VOC molecule

$[VOC]_0$ is input concentration of VOC molecules

- **CO_2 selectivity**

$$s_{CO_2}(\%) = \frac{[CO_2]}{[CO_2]+[CO]} \times 100$$

- **Specific input energy (SIE)**

$$SIE = \frac{P_{dis}}{Q_f} = \frac{\text{discharge power (W)}}{\text{gas flow rate (l/s)}} [J/l]$$

Properties of porous glass

plasma for environment protection

Catalyst support: borosilicate porous glass

- porosity #2, pore size 40 – 100 µm
- porosity #3, pore size 16 – 40 µm

Inner surface (BET):

- porosity #2: 0,130 m^2/g
- porosity #3: 0,350 m^2/g

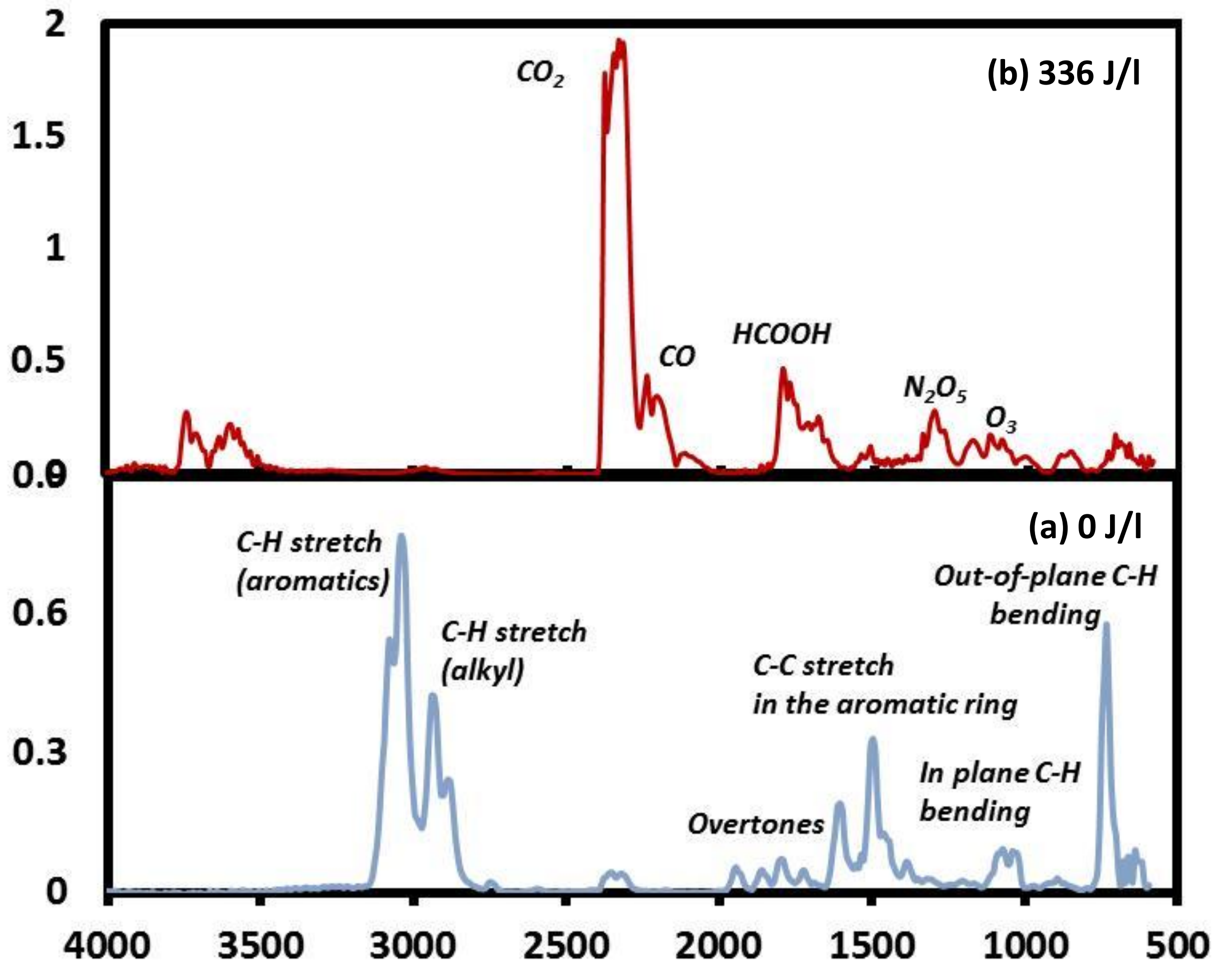
TiO2 film thickness:

500 cycles ~ 40 nm

1000 cycles ~ 80 nm

1500 cycles ~ 120 nm

FTIR spectra of reaction products in the DBD reactor with TiO2 catalyst

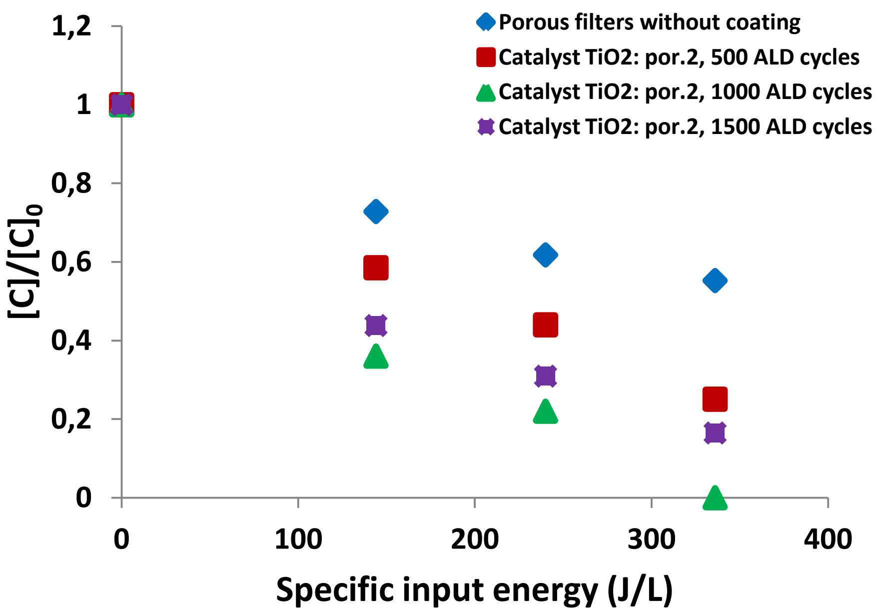


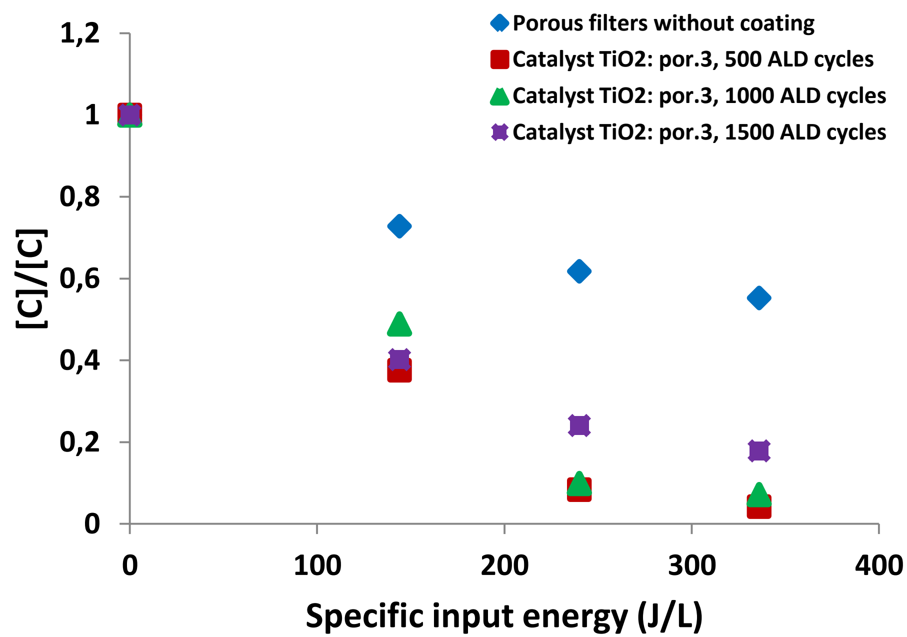
porosity 2,
1000 ALD cycles

toluene

Effectiveness of catalyst v. SIE

Relation between the removed amounts of toluene as a function of the specific input energy for different catalyst thickness and pore size



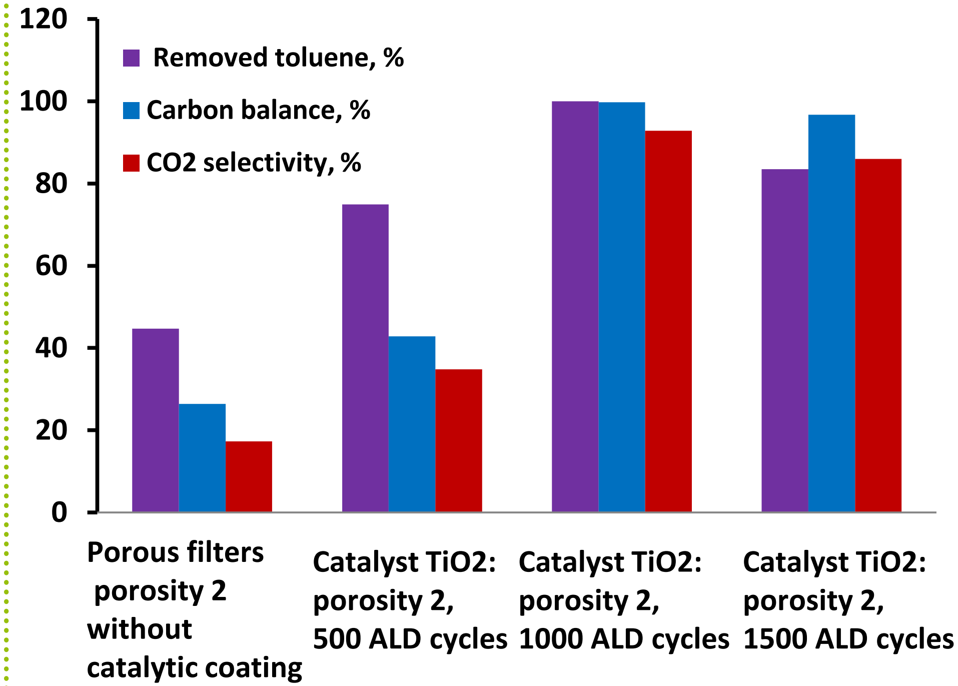


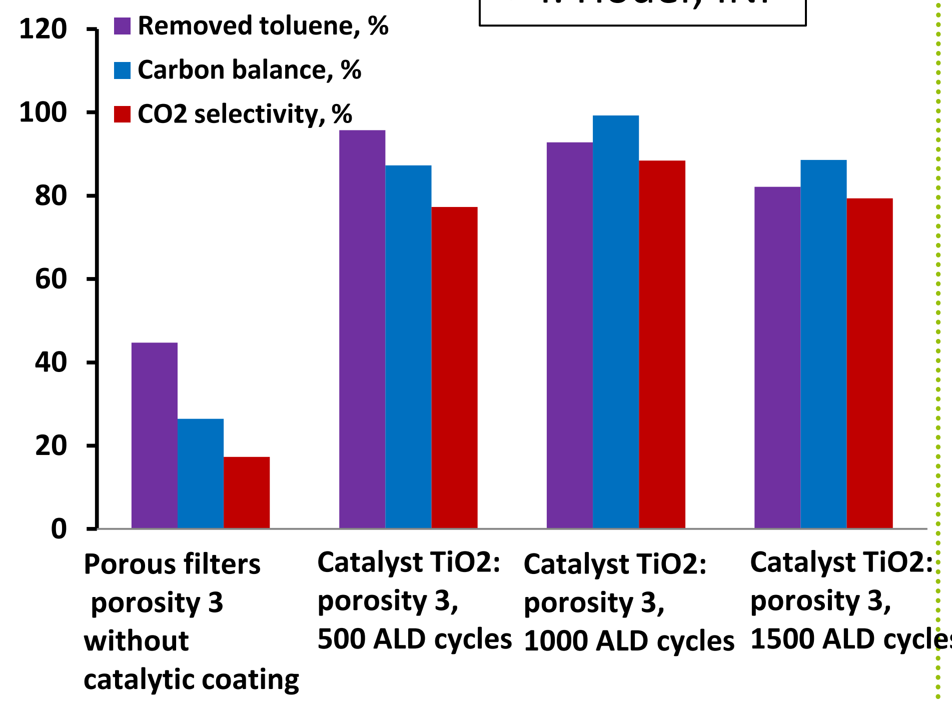
Activity of TiO2 catalysts during the destruction of 2500 ppm of toluene at 336 J/l total gas flow

-Plasma + catalyst removes much more VOCs than plasma alone

- Improves efficiency and selectivity

+ T. Höder, INP

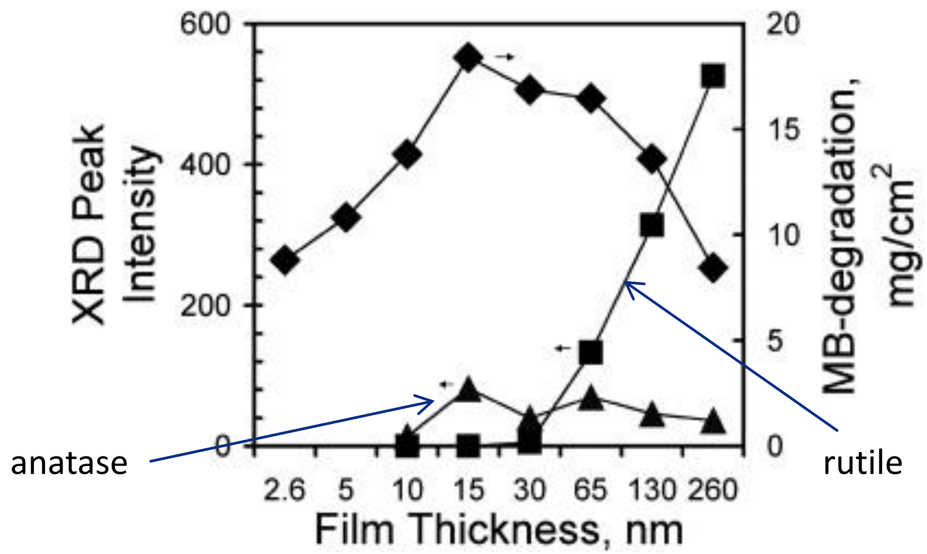




Best results with ~1000 ALD cycles, approximately 80 nm thick anatase

Compare with aqueous contamination removal

- **Methylene blue in water**
- **Maximum degradation rate at 15-100 nm film thickness**



* M.-L. Kääriäinen , T.O. Kääriäinen , D.C. Cameron Thin Solid Films Volume 517, Issue 24 2009 6666 – 6670

Effects of plasma and catalyst together

PlasTEP

plasma for environment protection

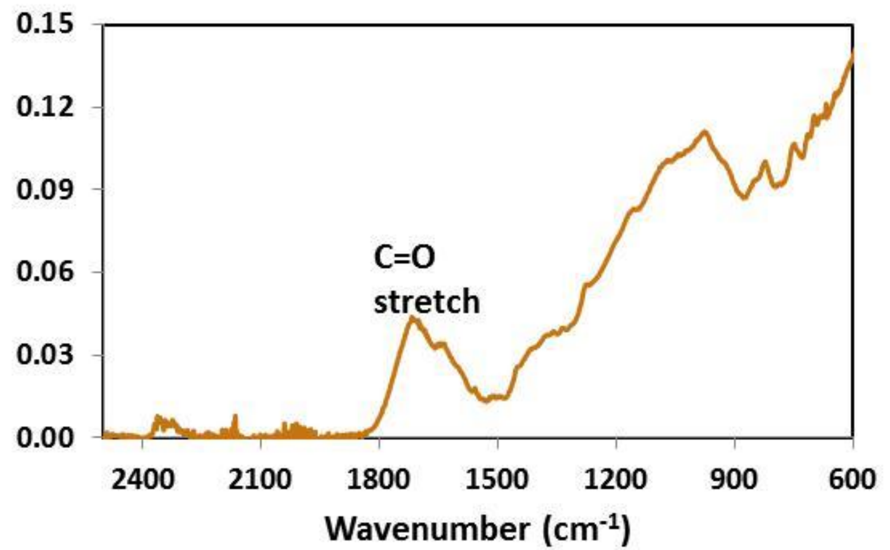
- Photogeneration of electrons and their chemical reactions
- Plasma-induced adsorption and desorption of contaminants and by-products
- Increased gas residence times by adsorption – more chance of a degradation reaction
- Modification of plasma properties by the catalyst
- Some local heating of the catalyst by the plasma
- Local intensification of the plasma discharge
- Modification of the mass transfer properties to the surface of the catalyst

Contamination

- Photocatalysts can generate reaction intermediates, which can accumulate on the active sites of the photocatalyst surface, resulting in a decrease in photocatalytic activity with time:

- Identified from FTIR signature

- Benzaldehyde and benzoic acid in toluene oxidation



- Possible periodic removal using oxygen plasma?

Summary

- Plasma catalytic reactors using anatase titanium dioxide significantly increase the efficiency of VOC removal over the use of plasma alone.
- Large catalyst area can be achieved by ALD coating of porous materials.
- FTIR spectra show the major reaction products of toluene in the DBD reactor are CO2 and CO.
- No carbon ring-retaining products were observed after the toluene passed through the DBD reactor with TiO_2coated catalyst under the correct conditions.
- The efficiency of toluene removal depends on the thickness of the catalyst (optimum ~80 nm) and the porosity of glass filters.

Thank you for your attention

Prof. David Cameron

LUT/ASTRaL

david.cameron@lut.fi

+358 294463548