



**1) How oxygen vacancies activate CO<sub>2</sub> dissociation on TiO<sub>2</sub> anatase (001)**

**2) Surface reactions of plasma-catalytic dry reforming of methane on anatase (001)**

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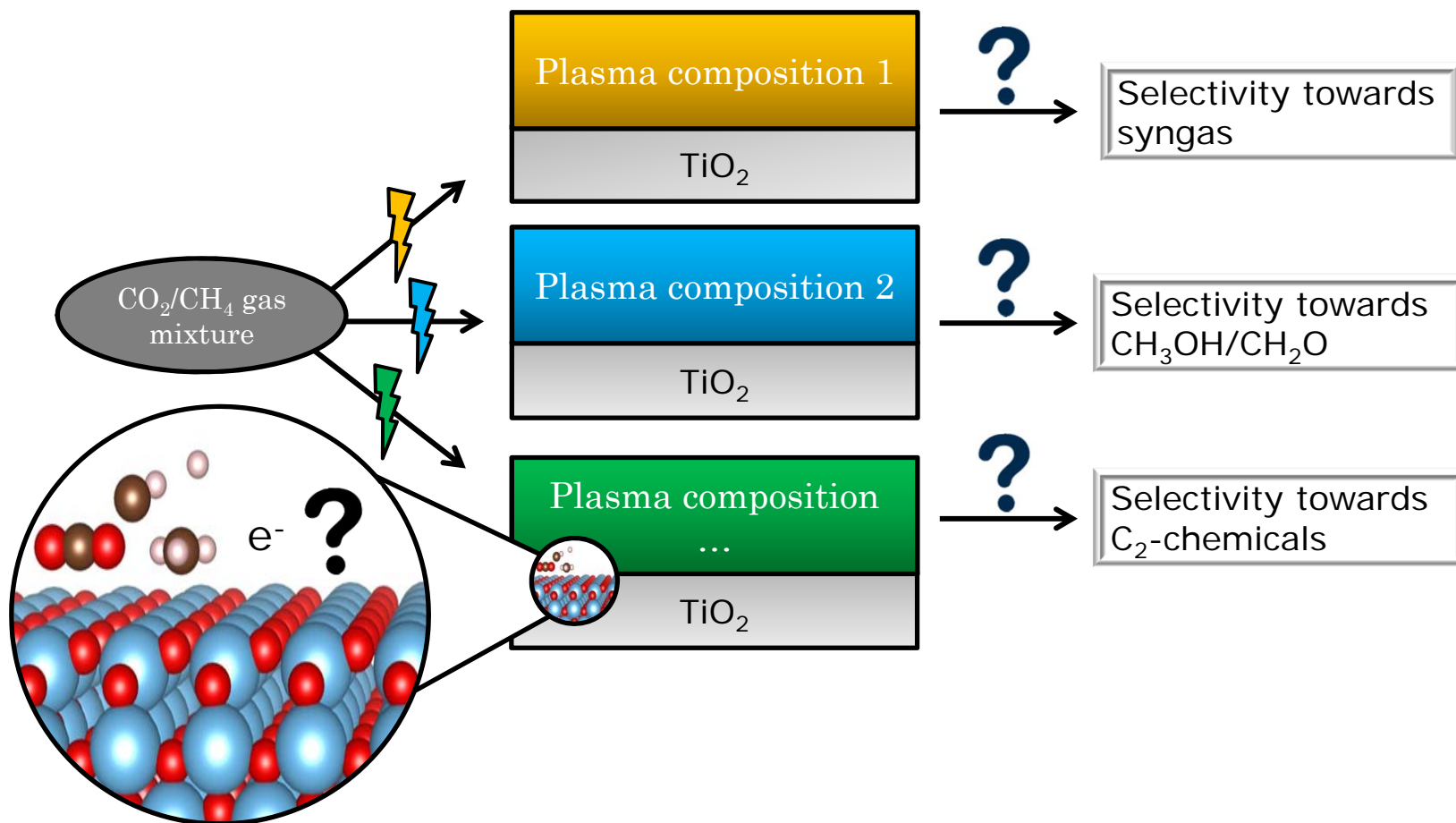


# Introduction

- The anthropogenic extension of the greenhouse effect
- Conversion of greenhouse gases to value-added chemicals
- Dry reforming of methane  
$$\text{CH}_4 + \text{CO}_2 \rightarrow 2 \text{CO} + 2 \text{H}_2$$
  - Syngas as feedstock for liquid fuels, oxygenated products, H<sub>2</sub>
- Challenges
  - High temperatures, sintering, Sulphur poisoning, coke formation



# Plasma surface interactions



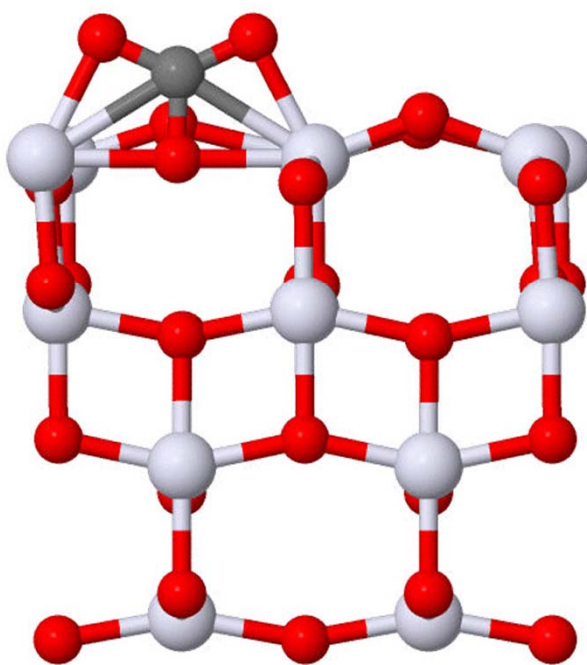


## CO<sub>2</sub> activation by oxygen vacancies

- Anatase (001)
  - High intrinsic Lewis basicity due to O 2sp states
- Strong chemisorbed CO<sub>2</sub>
  - Monodentated carbonate-like structure
  - Significant C-O bond weakening
    - Charge transfer, Bond elongation, Strong Vibrational red shift
- Oxygen vacancies
  - Increase of the Lewis basicity
  - New strong adsorption configurations

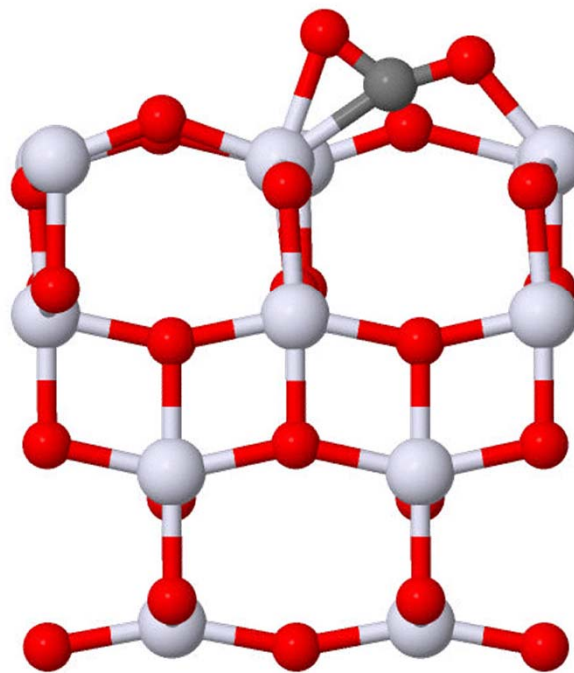


# CO<sub>2</sub> activation by oxygen vacancies



**5.03 eV**

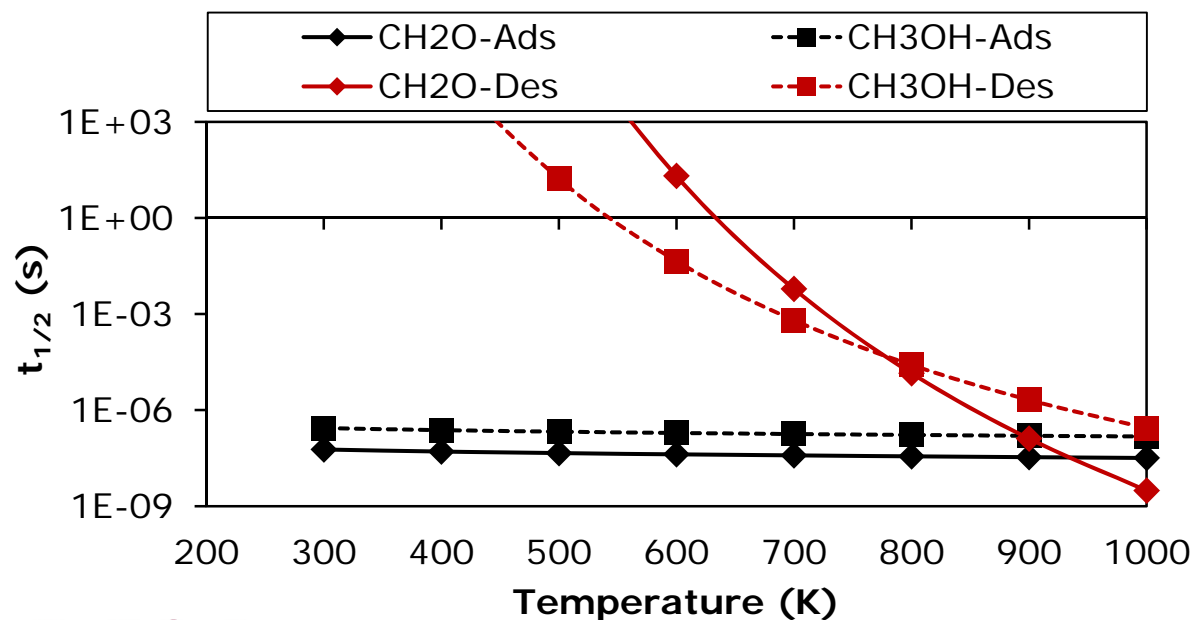
Stoichiometric





## Plasma-catalytic dry reforming

- Electron impact reactions generate  $\text{CH}_x$  and H radicals
- Readily available at the surface  $\text{CH}_3$ ,  $\text{CH}_2$  and H
- Formation of:
  - Methanol >600 K
  - Formaldehyde (Significant faster hydrogenation of  $\text{CH}_2$ )





## Conclusion

- Steer and control the plasma-catalytic dry reforming
- The composition of the end-products depends on:
  - Temperature
    - Different dependency of surface reactions
  - Plasma properties
    - Surface reactions depend on the available plasma species
    - Different plasma properties = Different plasma composition