Photocatalytic Synthesis of Hydrocarbons from CO_2/H_2O over Pd and Cu-Based Catalysts

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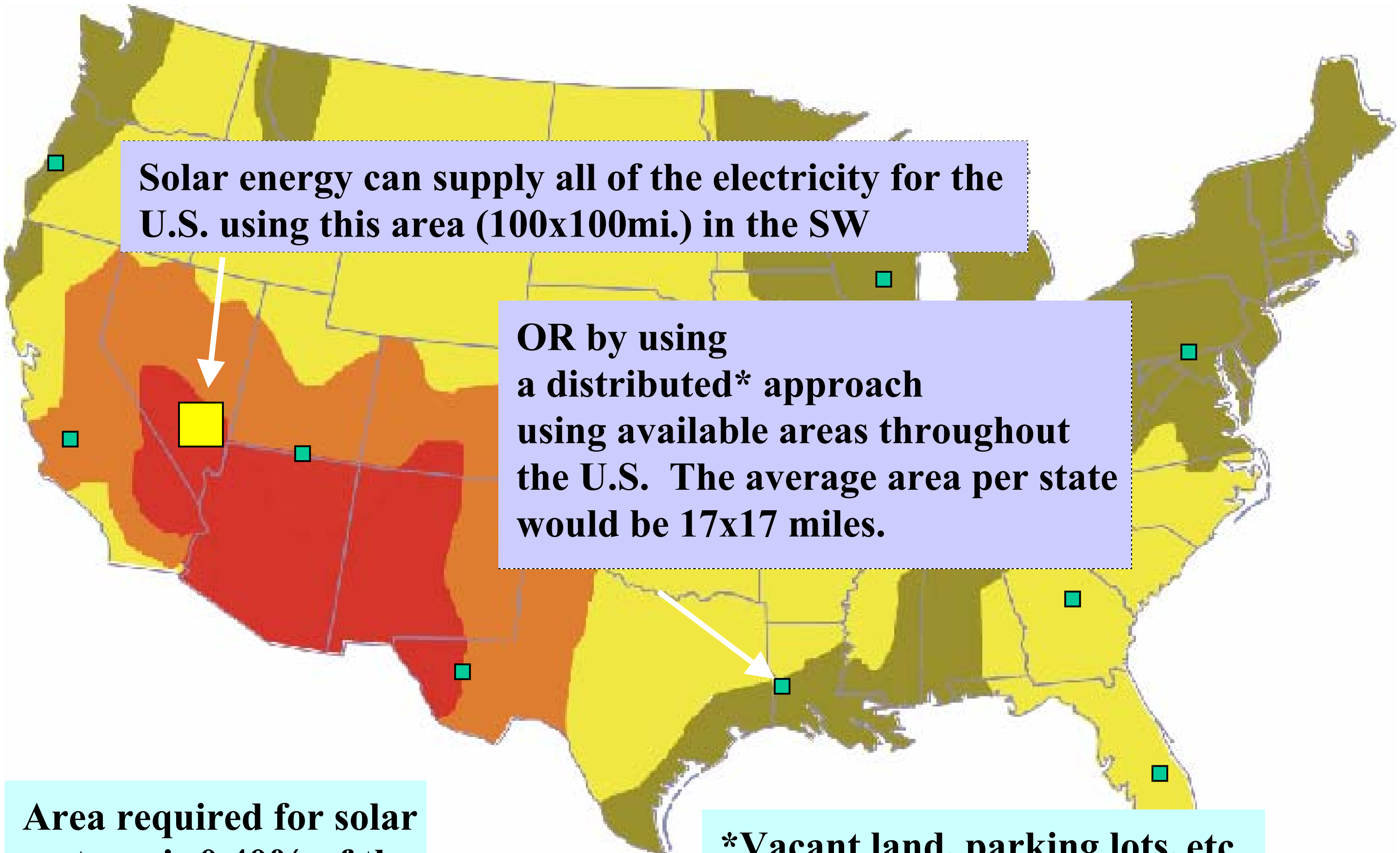
Introduction

Solar Energy ⟶ Solar Photovoltaic Electricity



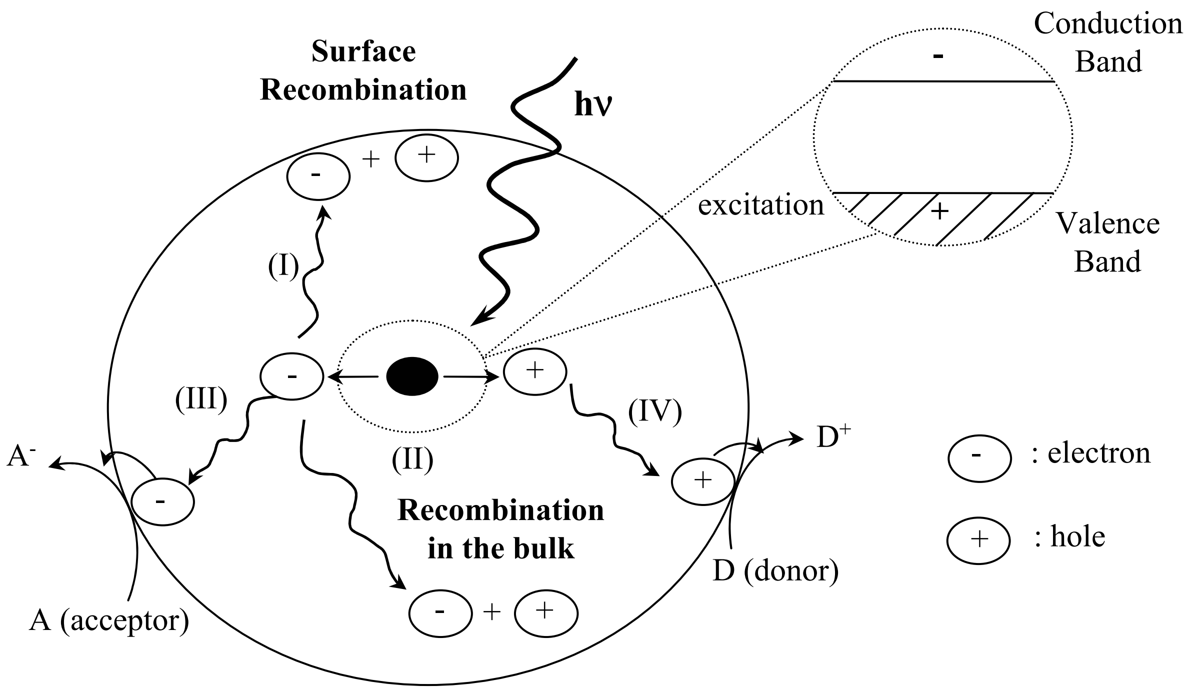
Solar energy can supply all of the electricity for the U.S. using this area (100x100mi.) in the SW

**OR by using
a distributed* approach
using available areas throughout
the U.S. The average area per state
would be 17x17 miles.**

Area required for solar systems is 0.40% of the continental U.S.

***Vacant land, parking lots, etc.**

Pathways of Electron/Hole Pairs and A and D Adsorbates



$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$ Oxidation potential = -0.812 V

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$$ Reduction potential = -0.244 V

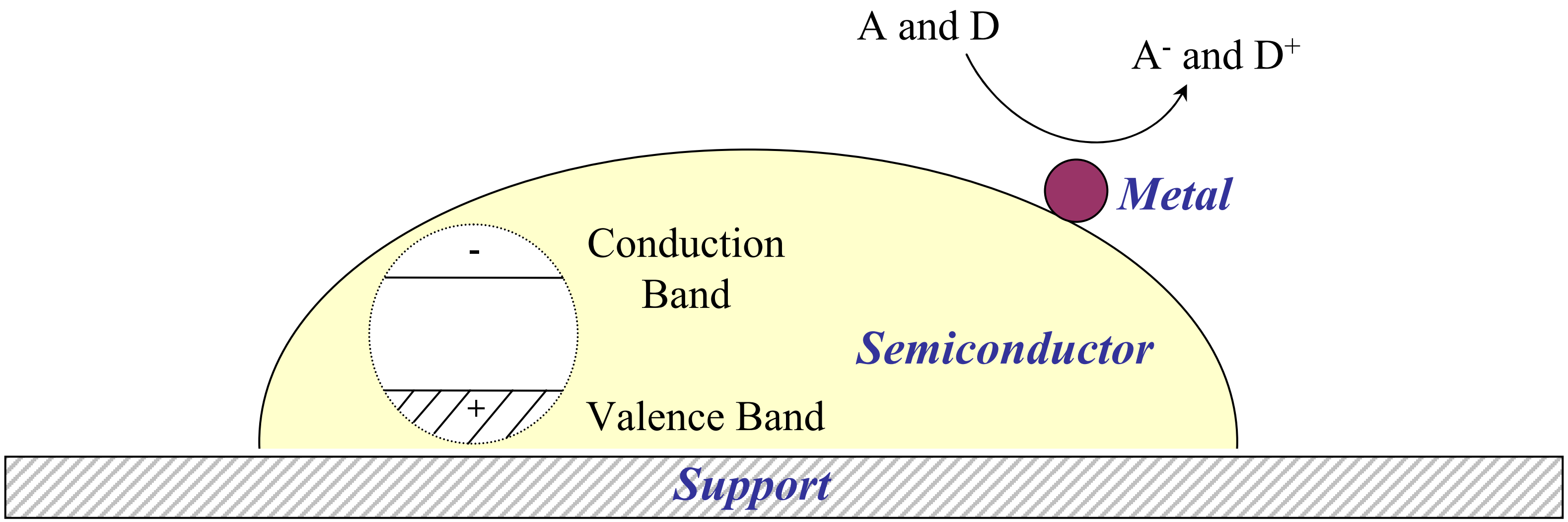
(I) SURFACE RECOMBINATION

(II) RECOMBINATION IN THE BULK

(III) DONATION OF ELECTRON TO ELECTRON ACCEPTOR SPECIES ON SURFACE

(IV) DONATION OF HOLE TO ELECTRON DONOR SPECIES ON SURFACE

Modification of Photocatalysts



Support – Surface area

Semiconductor – Band gap energy, Stability and Mobility of e^-/hole

Metal – Active sites

Objectives

- Screen catalysts by characterizing their activity and selectivity as well as stability for the CO_2/H_2O reaction under ambient conditions as a function of wavelength and intensity.

- Develop an in situ infrared (IR) technique to identify active adsorbates and elucidate reaction mechanism.

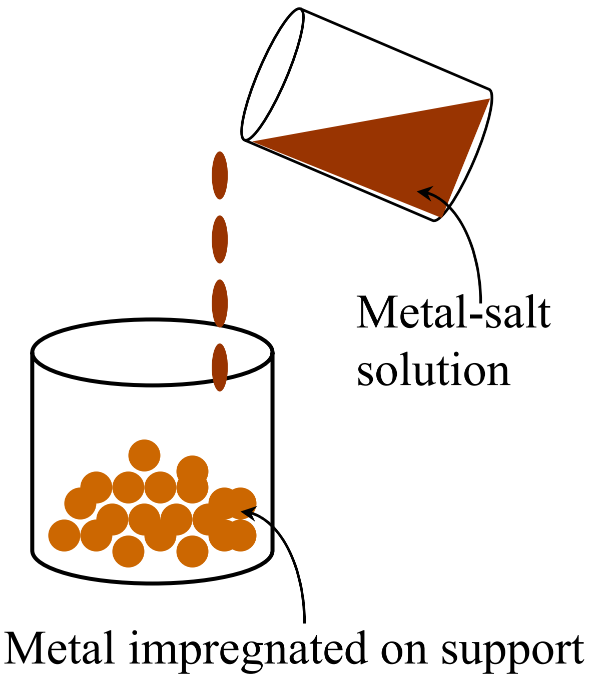
- Design new catalyst tailored to be stable, active, and selective in the visible light region.

Catalyst Preparation

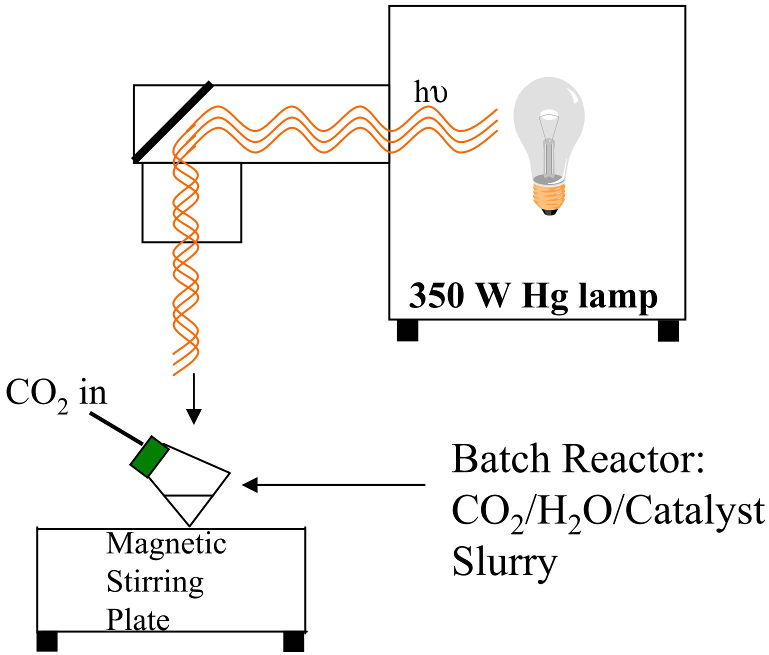
- Cu/TiO_2, Rh/TiO_2, Pd/SiC, Cu/SiC prepared by incipient wetness impregnation of support by metal-salt solution.

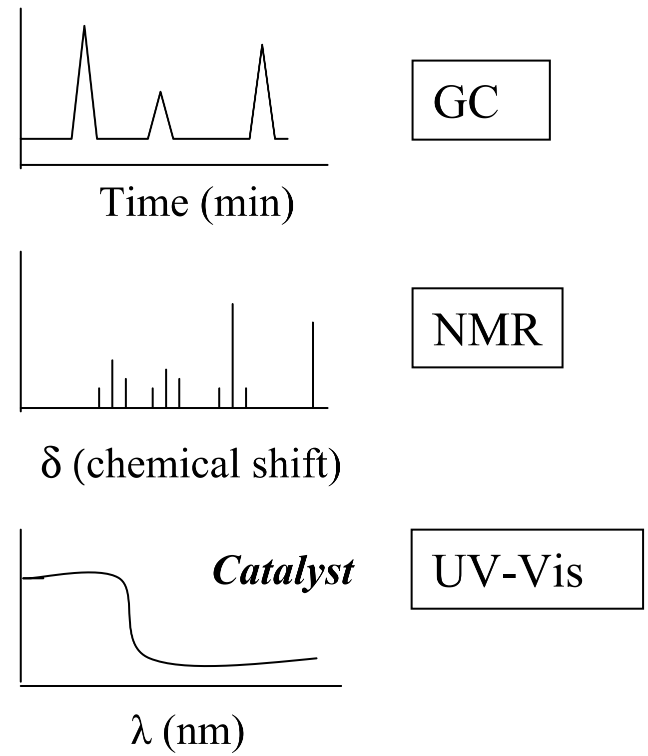
- Pd/TiO_2 sol gel prepared by adding $Ti(OC_4H_9)_4$ to a solution of n-butanol and acetic acid, followed by 8 hours of stirring, upon which $PdCl_2$ is added.

- All catalysts are subsequently calcined in flowing air at 773 K.



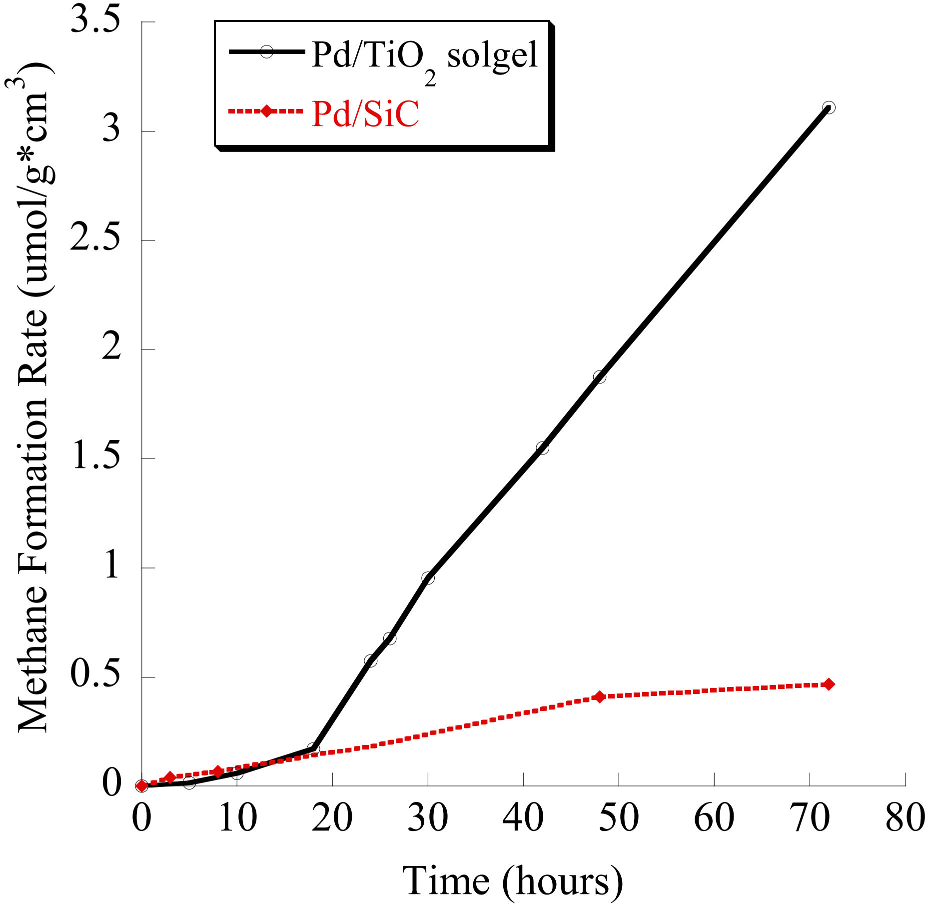
Experimental (slurry)





500 mg of Cu/TiO_2 sol gel, 10 ml of water
P = 0.1 MPa
T = 298 K
Pyrex glass cuts off the light < 260 nm

Methane Formation



Methane Formation Rate from Photocatalytic Reaction in Slurry Phase Reactor

Catalyst	Initial rate of CH_4 formation ($\mu mol/cm^3/hr/g_{cat}$)	Average rate of CH_4 formation ($\mu mol/cm^3/hr/g_{cat}$)
SiC	0.002	0.002
TiO_2	0.004	0.004
0.5 wt% Pd/SiC	0.013	0.010
2.0 wt% Pd/TiO_2 solgel	0.010	0.044
0.5 wt% Cu/SiC	0.011	0.008
0.5 wt% Cu/TiO_2	0.017	0.011
0.5 wt% Cu/$SrTiO_3$	0.006	0.006
0.5 wt% Rh/TiO_2	0.029	0.015

Quantum Efficiency

$$CO_2 + 2H_2O \xrightarrow{h\nu} CH_4 + 2O_2$$

$$C^{4+} \longrightarrow C^{4-}$$

$$\phi_Q\ (\%) = \frac{8 \text{ x moles of methane yield}}{\text{moles of UV photon absorbed by catalyst}} \text{ x } 100$$

UV-Visible Spectroscopy

Spectrum

IR → ← VISIBLE → ← UV →

Si CdSe GaP CdS SiC TiO_2 ZnS

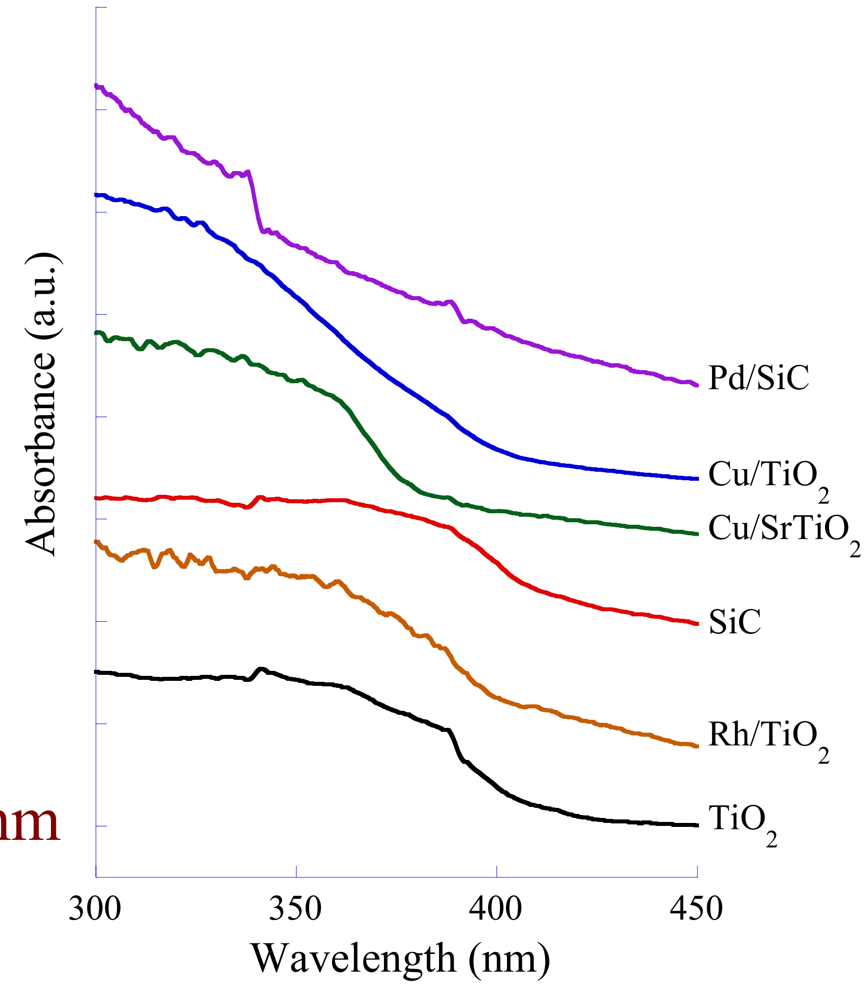
Semiconductors

λ (micrometers)

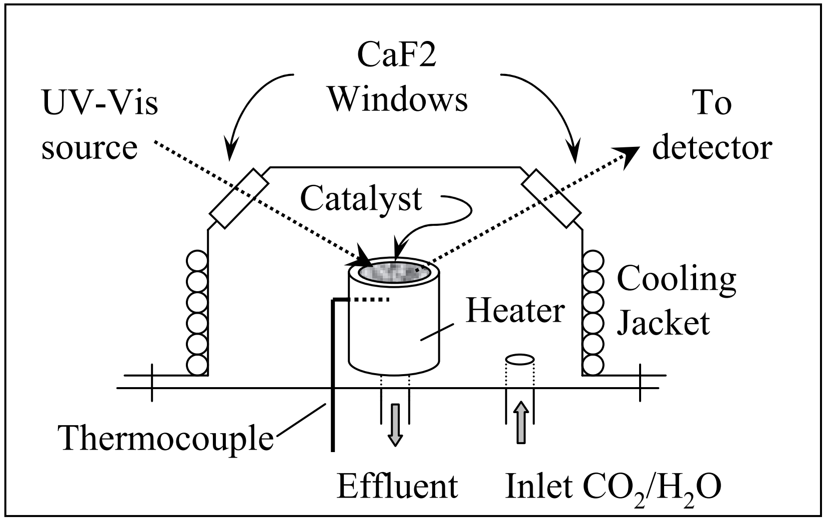
1.0	**0.78**	**0.62**	**0.52**	**0.44**	**0.39**	**0.34**	**0.31**
1.2	**1.6**	**2.0**	**2.4**	**2.8**	**3.2**	**3.6**	**4.0**

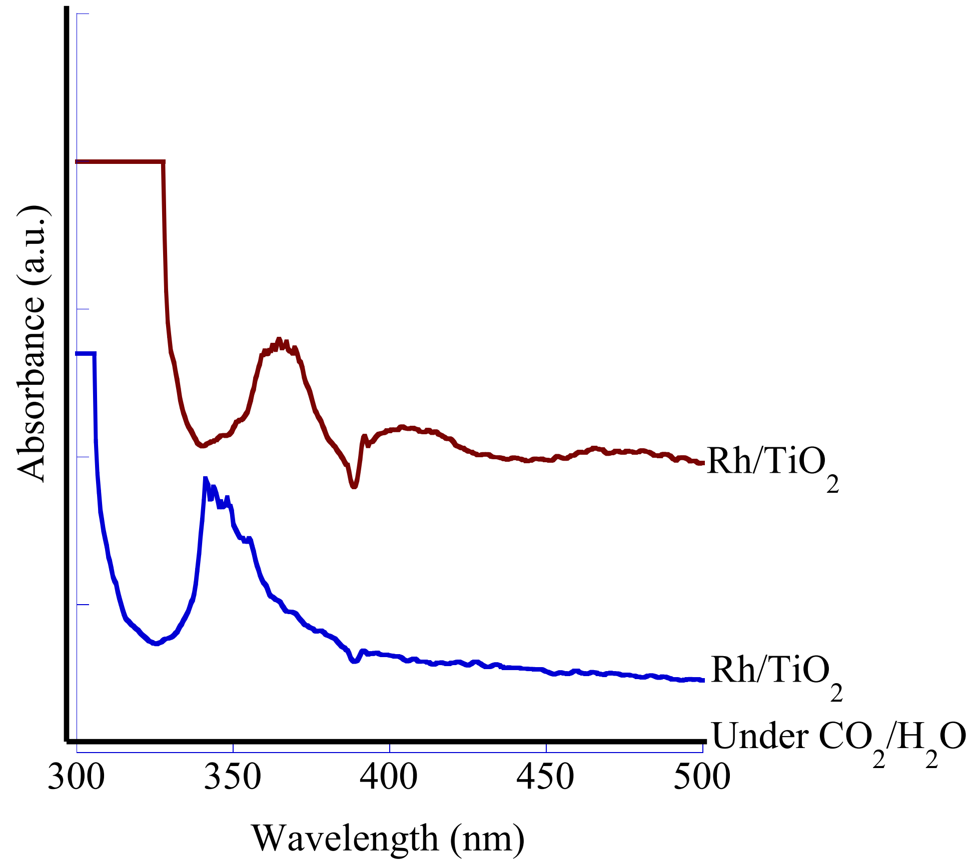
E_g (eV)

Pyrex glass cuts off the light < 260 nm



UV-Vis in CO_2/H_2O Environment





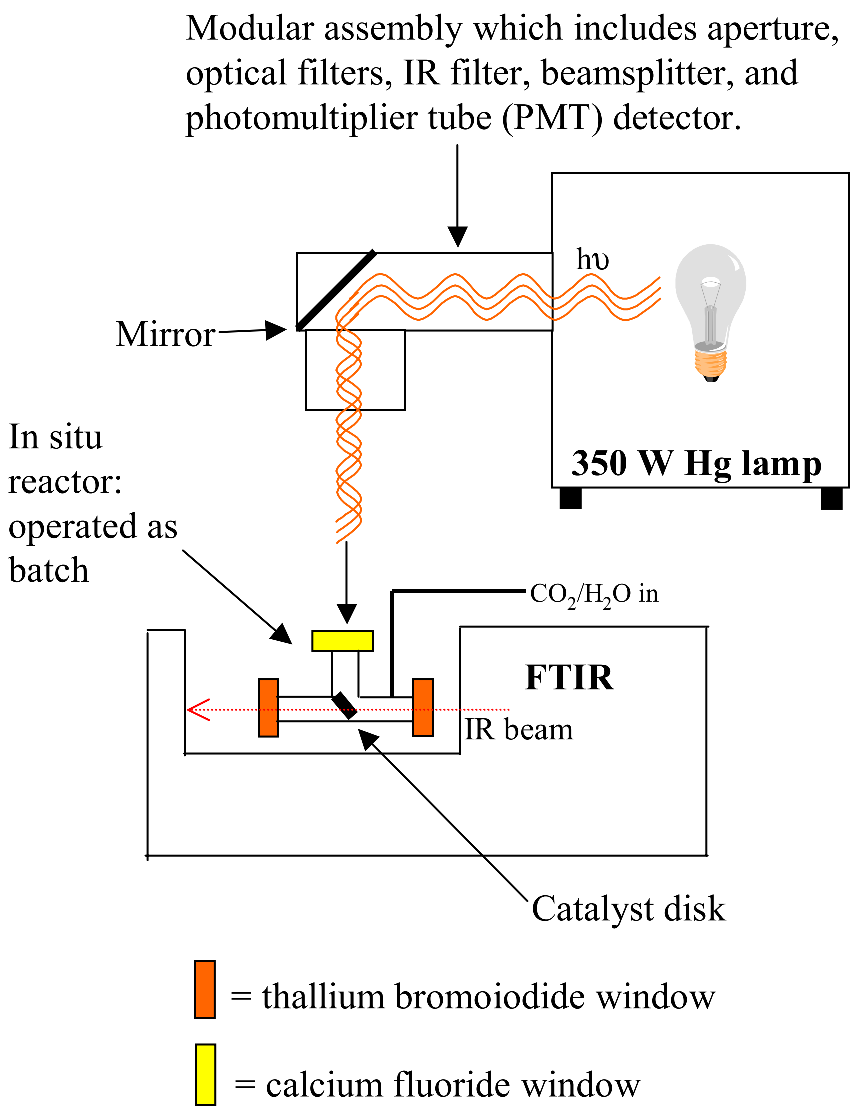
T = 303 K

CO_2 and H_2O vapor from the saturator

Quantum Efficiency (cont.)

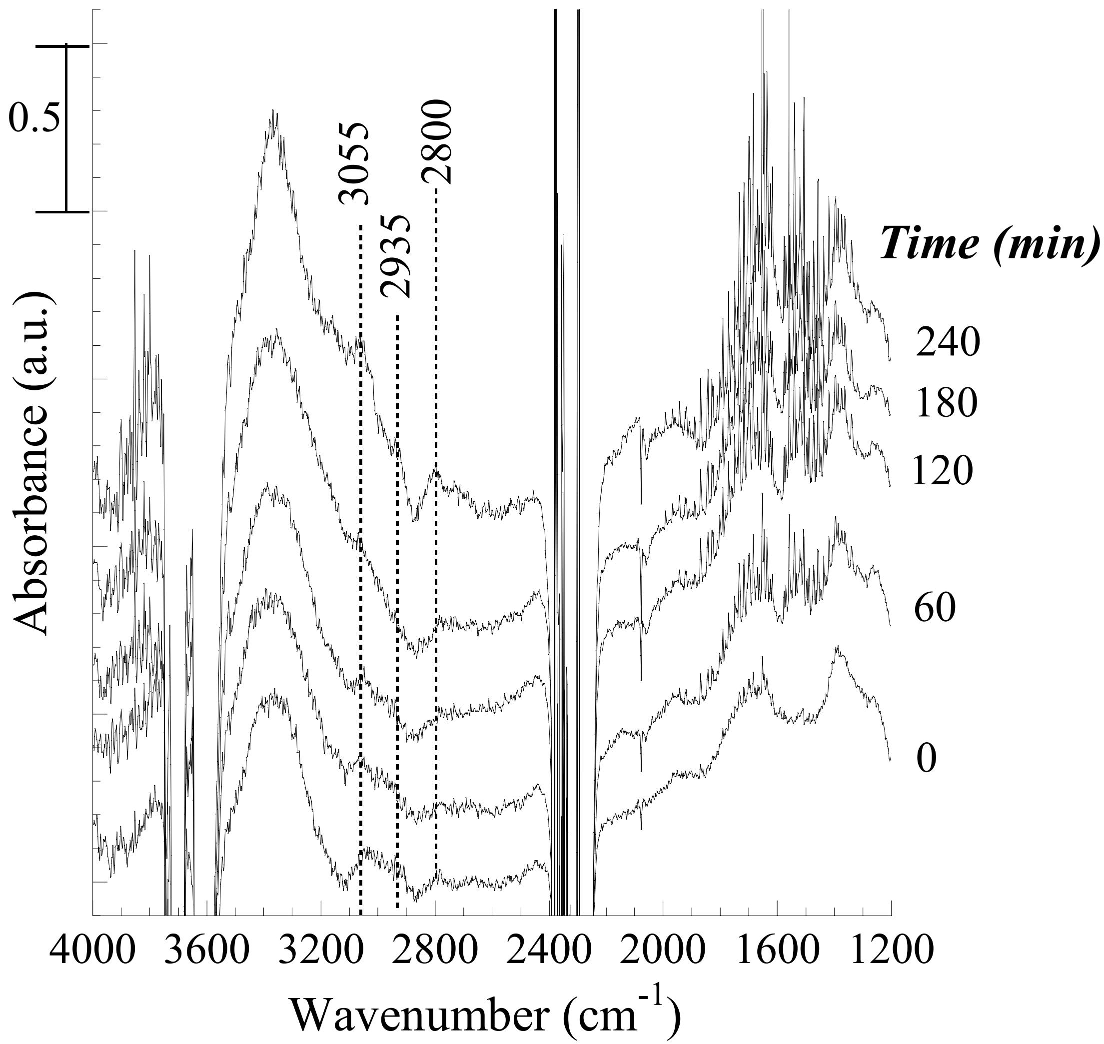
Catalyst	Quantum Efficiency (Φ_Q)
SiC	0.55
TiO_2	1.13
0.5 wt% Pd/SiC	3.96
2.0 wt% Pd/TiO_2 solgel	15.93
0.5 wt% Cu/SiC	3.11
0.5 wt% Cu/TiO_2	4.80
0.5 wt% Cu/$SrTiO_3$	1.94
0.5 wt% Rh/TiO_2	8.19

Experimental (in situ IR)



In situ IR Spectrum of Photocatalytic Reaction over Cu/TiO_2 with CO_2 and Water

$$CO_2 + H_2O \xrightarrow[Cu/TiO_2]{} HC + O_2$$

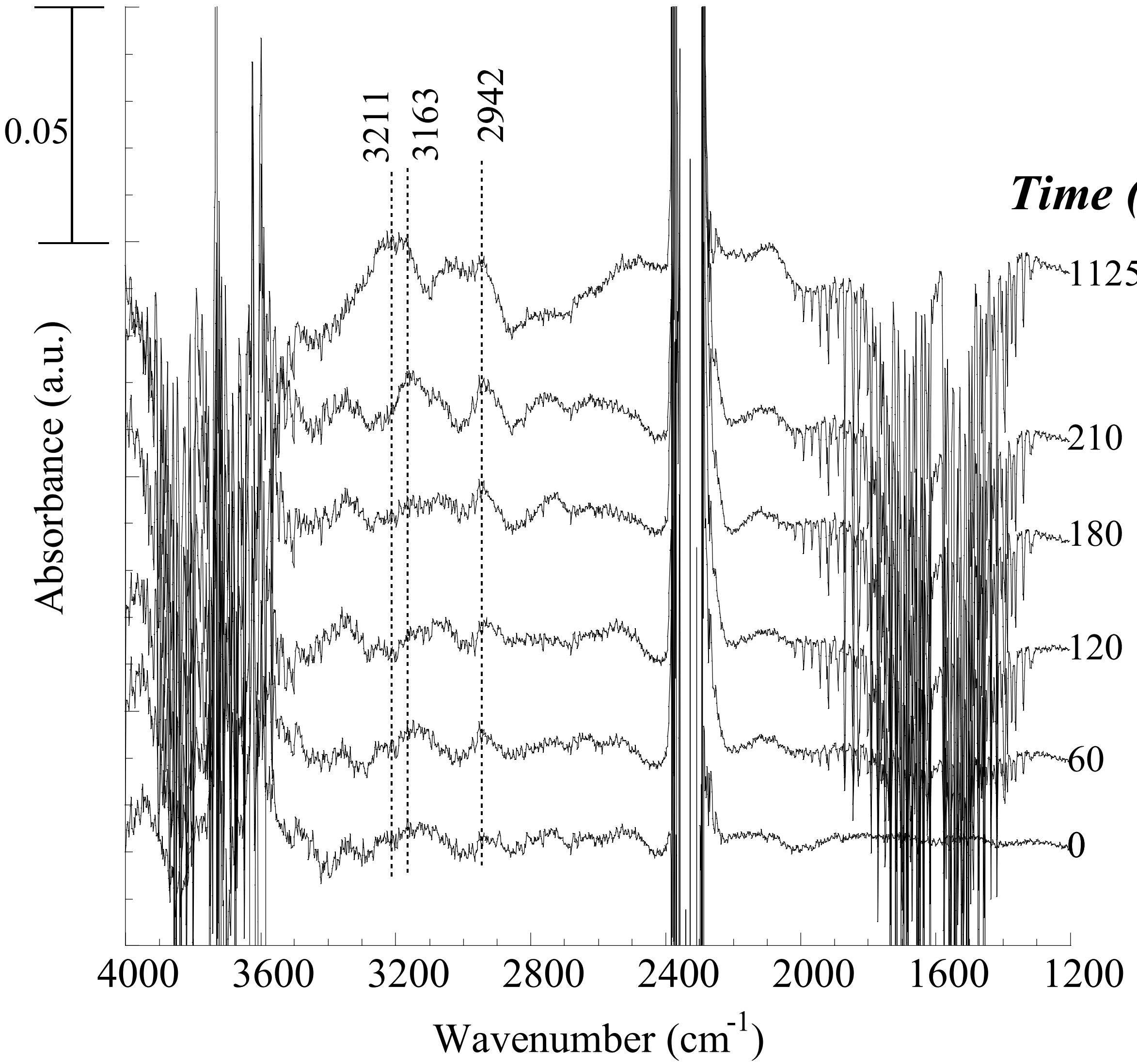


125 mg of Cu/TiO_2

P = 0.15 MPa, T = 303 K

In situ IR Spectrum of Photocatalytic Reaction over Rh/TiO_2 with CO_2 and Water

$$CO_2 + H_2O \xrightarrow[Rh/TiO_2]{} HC + O_2$$



125 mg of Rh/TiO_2

P = 0.15 MPa, T = 303 K

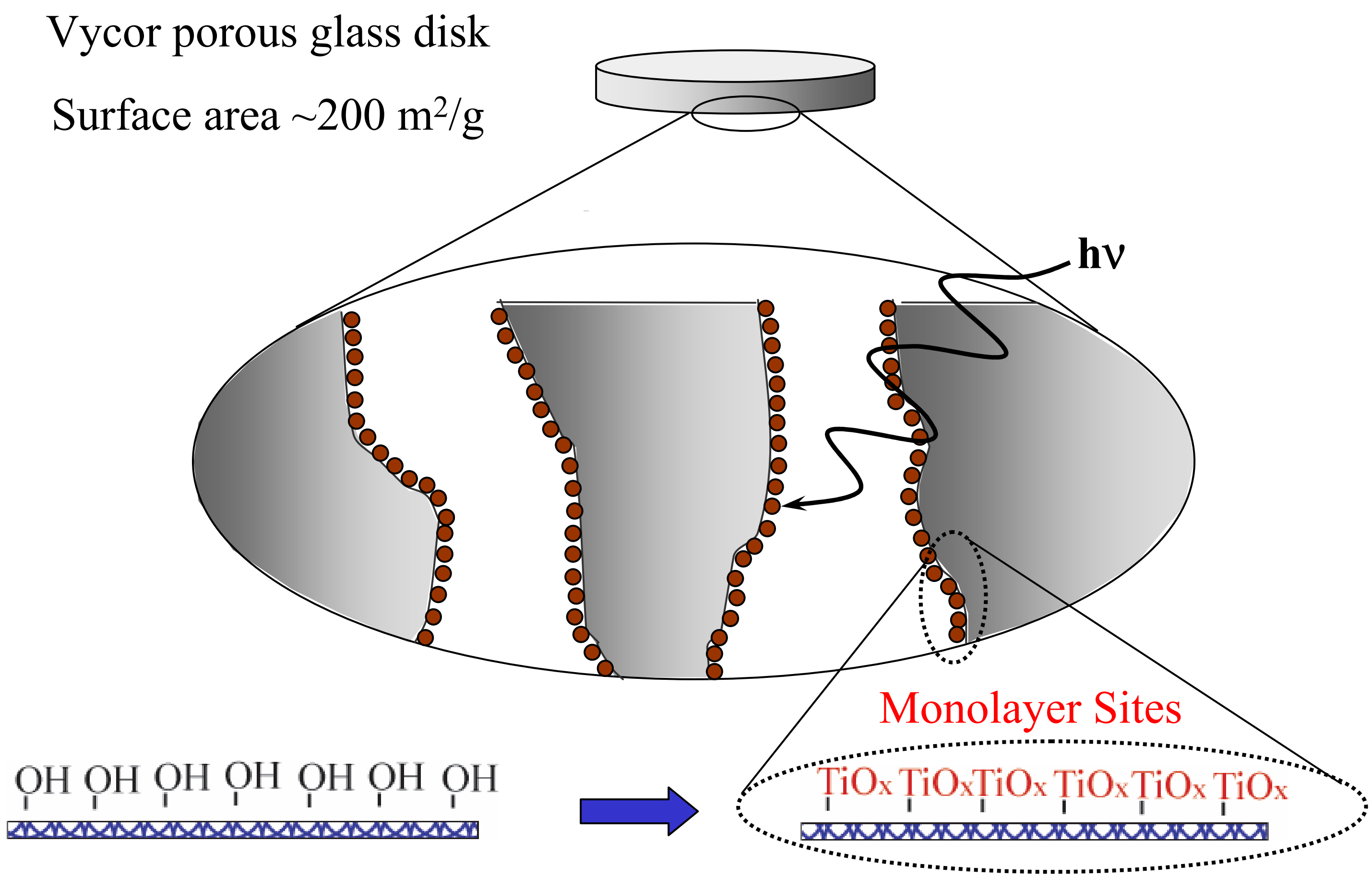
Conclusion

- The quantum efficiency calculations show that Pd/TiO_2 solgel is the best catalyst for methane formation. Rh/TiO_2 also exhibits high activity for this reaction.

- *In situ* UV-Visible studies reveals that TiO_2-supported catalysts require the higher energy (i.e. shorter wavelength) to pass through the water-thin film deposited on the surface to activate the photocatalytic reaction.

- Preliminary *in situ* IR could successfully monitor the adsorbate species.

Future Plan



$$\equiv SiOH + Ti(OCH_3)_4 \rightarrow \equiv SiO\text{-}Ti(OCH_3)_4 \xrightarrow{\text{Calcination}} \equiv SiO\text{-}TiO_x \xrightarrow{NH_3 \text{ doping}} \equiv SiO\text{-}TiN_y$$

Acknowledgement

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