Artificial Photosynthesis over TiO_2-Based Catalyst: Fact or Fiction?

Chieh-Chao Yang[1], Yi-Hui Yu[2], Bart v.d. Linden[1], Jeffery C.S. Wu[2], Guido Mul[1,3]

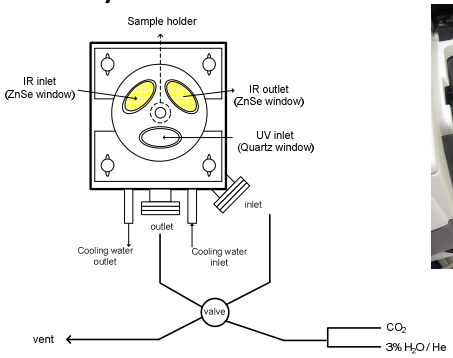
[1] *Catalysis Engineering, Chemical Engineering, Delft University of Technology*
[2] *Catalysis and Reaction Engineering Laboratory, Department of Chemical Engineering, National Taiwan University*
[3] *PhotoCatalytic Synthesis group, IMPACT Institute, University of Twente*
* c.c.yang@tudelft.nl, Tel: +31-15-2784396, Fax: +31-15-2785006

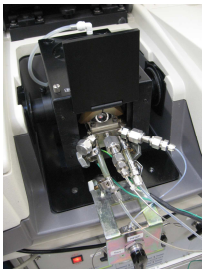
Introduction

Artificial photo-synthesis is the process to convert CO_2 into small molecule hydrocarbons by using light as energy source. Titania-based photocatalysts[1-4] are active in CO_2 reduction to CO , CH_4 and CH_3OH. The mechanism of CO_2 reduction has not been clarified yet. In this study, the nature of initial products in photocatalytic CO_2 reduction is discussed.

Experimental

- **DRIFTS system with three-window cell**





- **Pretreatment** - He, heat up to 393 K for 30min (for H_2O removal)
- **Reactants** - CO_2/He saturated with H_2O
- **light irradiation** -100W Hg lamp (λ: 250~600nm)

IR spectra were recorded every 10 mins.
(background spectra: catalyst with CO_2/H_2O adsorption)

- **Photocatalyst – 1% Cu(I)/TiO_2** **sol-gel method**

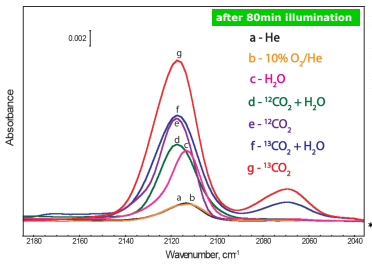
$Cu(NO_3)_2 \cdot 2.5\ H_2O$
HNO_3
TBOT (titanium tetrabutoxide)
PEG (polyethylene glycol)
→ thermal hydrolysis → precursor → calcination (423 K for 3h, 773 K for 5h) → **Cu(I)/TiO_2**

* Based on XPS results, the majority of copper on the surface is Cu(I).

- **Addition carbon to Cu(I)/TiO_2 (coking procedure)**

introducing 1%C_4H_{10} and 50%CO_2 flow (30mL/min) over Cu(I)/TiO_2 and heat up to 873K.

- **Illumination in different conditions**

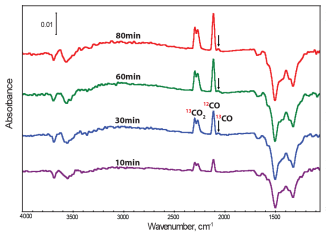


- **Cu (I) → sites for CO adsorption.**
- **H_2O induced CO formation (2117cm^{-1}).**
- **^{13}CO (2069cm^{-1}) formed together with ^{12}CO (2117cm^{-1}) in the presence of $^{13}CO_2$ (w/H_2O).**

* bkg spectra: catalyst in respective atmosphere.

Results

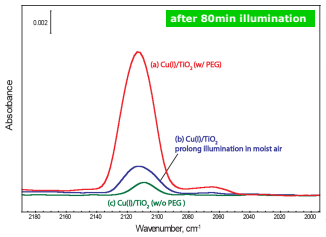
- **Illumination of Cu(I)/TiO_2 preloaded with $^{13}CO_2$**



- **During illumination, ^{13}Carbonates decomposed (1200-1800cm^{-1}) mainly into $^{13}CO_2$ (2280cm^{-1}), and very little ^{13}CO (2067cm^{-1}).**
- **hydroxyl-group and surface adsorbed water involved in CO formation. (3000-4000cm^{-1})**
- **^{12}CO (2115cm^{-1}) still predominately formed.**

* bkg spectra: Cu(I)/TiO_2 preloaded with $^{13}CO_2$.

- **Carbon assisted photocatalytic CO_2 reduction**



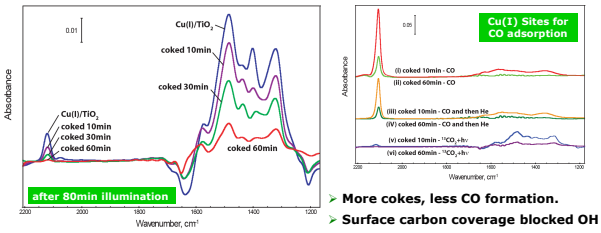
- **After prolonged illumination in humid air, CO formation largely decreased.**
- **Without PEG addition in synthesis, much less CO formed by illumination.**

$$H_2O + {}^{12}C \xrightarrow{h\nu} {}^{12}CO + H_2$$

$$^{13}CO_2 + {}^{12}C \xrightarrow{h\nu} {}^{13}CO + {}^{12}CO$$

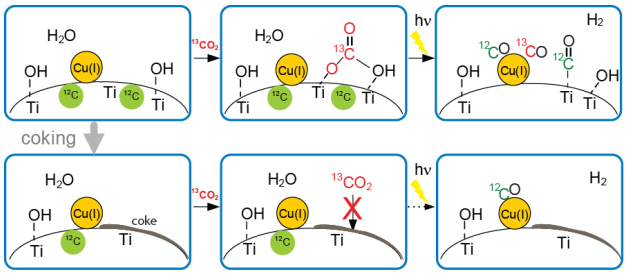
* bkg spectra: respective catalysts preloaded with $^{13}CO_2$.

- **"extra" carbon addition to Cu(I)/TiO_2**



- **More cokes, less CO formation.**
- **Surface carbon coverage blocked OH sites and further CO formation, but not Cu(I).**

- **Chemistry on Cu(I)/TiO_2 during illumination**



Conclusions

- **In-situ DRIFTS experiments successfully probed the catalyst surface during photocatalytic CO_2 reduction.**
- **Carbon residues, which formed during synthesis procedure (PEG), greatly participated in the formation of CO over Cu-promoted TiO_2.**
- **The removal of carbon residues by prolonged exposure to water vapor is more efficient than thermal activation (calcination).**
- **Coking of Cu(I)/TiO_2 showed that extensive carbon coverage diminished CO formation during illumination in the presence of CO_2.**
- **H_2O induced photocatalytic gasification of carbon residues should be carefully considered for the evaluation of CO_2 photoreduction.**

References

[1] K. Adachi et al., *Solar Energy* 53 (1994) 187.
[2] I.-H. Tseng et al., *Appl. Catal. B.* 37 (2002) 37.
[3] M. Anpo et al., *J. Electroanalytic Chem.* 396 (1995) 21.
[4] F. Saladin et al., *J. Chem. Soc., Chem. Commun.* 5 (1995) 533.

Acknowledgment

- The authors gratefully thank to the support from **ACTS** (NWO, the Netherlands), in the framework of an **NSC-NWO project.**

TU Delft Delft University of Technology

Challenge the future