

**CO<sub>2</sub> Sequestration and Recycle by Photocatalysis  
with Visible Light**

Technical Progress Report

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Steven S. C. Chuang  
Department of Chemical Engineering  
The University of Akron  
Akron, OH 44325-3906

Tel: 330-972-6993  
Fax: 330-972-5856  
Email: [schuang@uakron.edu](mailto:schuang@uakron.edu)

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## ABSTRACT

Photocatalysis could provide a cost-effective route to recycle CO<sub>2</sub> to useful chemicals or fuels. Development of an effective catalyst for the photocatalytic synthesis requires (i) the knowledge of the surface band gap and its relation to the surface structure, (ii) the reactivity of adsorbates and their reaction pathways, and (iii) the ability to manipulate the active site for adsorption, surface reaction, and electron transfer.

The research tasks accomplished during first six months include setting up a photo-catalytic reactor, optical bench, calibration of gas chromatograph, catalyst preparation, and catalyst screening study. Addition of Pt and Cu on TiO<sub>2</sub> was found to increase the activity of TiO<sub>2</sub> catalysts for the synthesis of methanol and methane. The most active catalysts obtained from this study will be used for mechanistic study.

The overall goal of this research is to provide a greater predictive capability for the design of visible light-photosynthesis catalysts by a deeper understanding of the reaction kinetics and mechanism as well as by better control of the coordination/chemical environment of active sites.

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## INTRODUCTION

CO<sub>2</sub> emission has become a worldwide problem due to its potential impact on global climate. Artificial photosynthesis is one of the potential approaches to reduce CO<sub>2</sub> emissions. There has been much on-going research to develop photochemical processes that can activate thermodynamically stable molecules, i.e., CO<sub>2</sub>, H<sub>2</sub>O, and CH<sub>4</sub>, and convert them to CH<sub>3</sub>OH or other valuable chemicals. Most of these studies have utilized ultraviolet (UV) light to activate the catalyst; the reaction processes have suffered from low efficiencies, catalyst instability, and deactivation. Additionally, the required use of UV light to excite valence electrons makes the process prohibitively expensive for the utilization of CO<sub>2</sub> as a feedstock for the synthesis of chemicals and fuels.

A practical and effective photocatalyst for the reaction CO<sub>2</sub> with H<sub>2</sub>O must possess: (i) the ability to excite valence electrons with visible light, (ii) a high activity/selectivity toward CH<sub>3</sub>OH and hydrocarbons, and (iii) catalyst stability. No catalyst has been identified that exhibits both promising activity and stability during photosynthesis of CO<sub>2</sub> and H<sub>2</sub>O to form CH<sub>3</sub>OH or CH<sub>4</sub>. The key to developing an efficient catalyst to utilize visible light lies in our understanding of the reaction mechanism, which will provide a scientific basis for catalyst design. In first six months of this research project period, we have focused our effort in design of experimental system for photo-catalytic reaction and preparation of catalysts. Preliminary testing showed that TiO<sub>2</sub> exhibited the activity for catalyzing CH<sub>4</sub> and CH<sub>3</sub>OH formation from CO<sub>2</sub>/H<sub>2</sub>O. Addition of Pt and Cu on TiO<sub>2</sub> was found to further increase the activity of TiO<sub>2</sub> catalysts for the synthesis of methanol and methane.

The overall goal of our long-term research is to provide a greater predictive capability for the design of visible light-photosynthesis catalysts by a deeper

understanding of the reaction kinetics and mechanism as well as by better control of the coordination/chemical environment of active sites.

## **EXPERIMENTAL**

### **Catalyst Preparation**

TiO<sub>2</sub> used in this study is P-25 from Degussa. 0.5 wt% Pt/TiO<sub>2</sub> and 0.5 wt% Cu/TiO<sub>2</sub> were prepared by the incipient wetness method using respective metal-salt aqueous solutions. The ratio of the volume of solution to the weight of the support was approximately 1 cc to 1 g. The catalysts were dried overnight at room temperature, heated from room temperature to 673 K with a rate of 2-3 K/min followed by calcination in air at 673 K for four hours and subsequently reduced in flowing hydrogen at 673 K for three hours.

### **Reaction Study**

Figure 1 shows the experimental apparatus with slurry phase reactor setup. A 25 ml Pyrex Erlenmeyer flask with tube in tube metal fitting was used as the reactor to determine the catalyst activity. Each reaction run employed 10 ml H<sub>2</sub>O, 15 ml CO<sub>2</sub>, and 500 mg catalyst. The CO<sub>2</sub> gas was bubbled through the mixture for 15 minutes and then the system was pressurized to 20 psig and sealed. The mixture was stirred continuously at 298 K and exposed to UV/visible light radiation under 225 mW/cm<sup>2</sup> intensity for different duration of time.

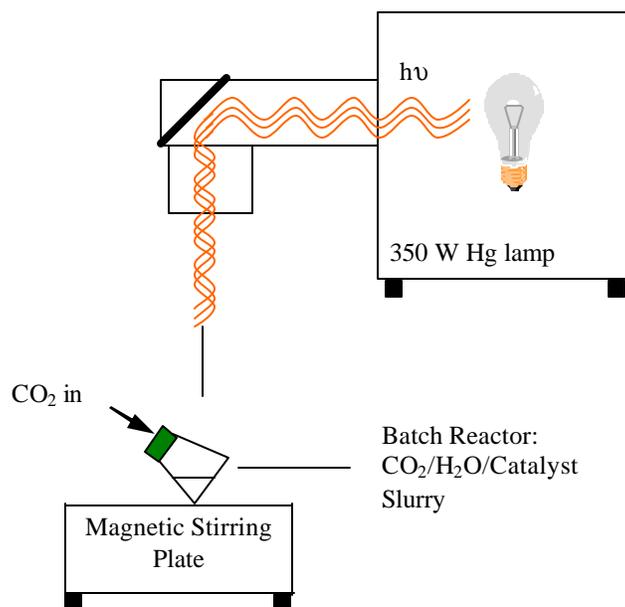
The catalysts have been tested under full visible and UV light radiation under 225 mW/cm<sup>2</sup> intensity at room temperature and atmospheric pressure. The liquid products were sampled and analyzed via GC (HP 5890A with 80/100 PORAPAK-Q column) to determine the hydrocarbon and methanol compositions.

## RESULTS AND DISCUSSION

Table 1 lists the rate of product formation of the photocatalytic reaction of  $\text{CO}_2/\text{H}_2\text{O}$  that was carried out with a mixture of catalyst and liquid water in a batch reactor at 298 K.  $\text{TiO}_2$  exhibited the activity for catalyzing  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$  formation from  $\text{CO}_2/\text{H}_2\text{O}$ . Addition of Pt and Cu on  $\text{TiO}_2$  further increased the activity of  $\text{TiO}_2$  catalysts for the synthesis of methanol and methane.

## CONCLUSIONS

The efforts in the first 6 months of the project was devoted to the design of the photo-catalytic reactor system, purchase of components, testing of the reactor system, calibration, catalyst preparation, and preliminary testing of the catalysts. The results showed that  $\text{TiO}_2$  exhibited the activity for catalyzing  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$  formation from  $\text{CO}_2/\text{H}_2\text{O}$ . Addition of Pt and Cu on  $\text{TiO}_2$  was found to further increase the activity of  $\text{TiO}_2$  catalysts for the synthesis of methanol and methane. A series of  $\text{TiO}_2$  based catalysts including 0.5 wt% Rh/ $\text{TiO}_2$ , and 0.5 wt% Cu/ $\text{SrTiO}_3$ , and Ti silsesquioxane  $\text{Ti}(\text{O}-i\text{Pr})\{(\text{c}-\text{C}_5\text{H}_5)_7\text{Si}_7\text{O}_{12}\}$  will be tested to determine the feasibility of using  $\text{TiO}_2$ -based catalysts for the synthesis of  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$  from  $\text{CO}_2/\text{H}_2\text{O}$ .



**Fig. 1. Experimental apparatus**

**Table 1. Photosynthesis of Hydrocarbons and Methanol from CO<sub>2</sub>/H<sub>2</sub>O.**

Catalyst	Gas-Phase Product	Liquid-Phase Product	Initial Rate C <sub>1</sub> HC (μmol/hr/g <sub>cat</sub> )	Initial Rate C <sub>2+</sub> HC (μmol/hr/g <sub>cat</sub> )	Final Rate C <sub>1</sub> HC (μmol/hr/g <sub>cat</sub> )	Final Rate C <sub>2+</sub> HC (μmol/hr/g <sub>cat</sub> )	Avg. Rate MeOH (μmol/hr/g <sub>cat</sub> )
0.5 wt% Pt/TiO <sub>2</sub>	C <sub>1</sub> -C <sub>2</sub>	MeOH	1.1	.54	--	--	85.8
TiO <sub>2</sub>	C <sub>1</sub>	MeOH	--	--	.01	--	47.5
0.5 wt% Cu/TiO <sub>2</sub>	C <sub>1</sub> -C <sub>3</sub>	MeOH	.09	.42	.002	-.004	80.0

Initial Rate = The rate of production at the onset of reaction, typically 0.5-2 hr, as determined by GC analysis.

Final Rate = The rate of production between the final two sample times as determined by GC analysis.

Typical Reaction Conditions: 10 mL H<sub>2</sub>O (l), 20 mL CO<sub>2</sub> (g), 500 mg cat., 298 K, 0.1 MPa.