CO₂ Sequestration and Recycle by Photocatalysis

with Visible Light

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ABSTRACT

Visible light-photocatalysis could provide a cost-effective route to recycle CO₂ 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 objective of this research is to study the photo-catalytic activity of TiO₂-based catalyst. A series of TiO₂-supported metal catalysts were prepared for determining the activity and selectivity for the synthesis of methane and methanol. 0.5 wt% Cu/SrTiO₃ was found to be the most active and selective catalyst for methanol synthesis. The activity of the catalyst decreased in the order: Ti silsesquioxane > Cu/SrTiO₃ > Pt/TiO₂ > Cu/TiO₂ > TiO₂ > Rh/TiO₂. To further increase the number of sites for the reaction, we propose to prepare monolayer and multilayer TiO_x on high surface area mesoporous oxides. These catalysts will be used for in situ IR study in the Phase II research project to determine the reactivity of adsorbates. Identification of active adsorbates and sites will allow incorporation of acid/basic sites to alter the nature of CO₂ and H₂O adsorbates and with Pt/Cu sites to direct reaction pathways of surface intermediates, enhancing the overall activity and selectivity for methanol and hydrocarbon synthesis.

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

CO₂ emission has become a worldwide problem due to its potential impact on global climate. A wide range of CO₂ mitigation technologies have been proposed (1); they are listed in Table 1. Each group of technologies has the disadvantage of either a limited impact or a high operating cost. The group of CO₂ mitigation technologies termed “Least Regrets” are the least costly and may meet short-term goals, however, they suffer from a limited reduction potential. CO₂ capture/sequestration, nuclear power, and extensive use of renewable energy have the potential to significantly reduce CO₂ emissions, but their operating costs are substantially higher.

One promising alternative to these technologies is artificial photosynthesis. There has been much on-going research to develop photochemical processes that can activate thermodynamically stable molecules, i.e., CO₂, H₂O, and CH₄, and convert them to CH₃OH or other valuable chemicals (2-10). 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 CO₂ as a feedstock for the synthesis of chemicals and fuels.

A practical and effective photocatalyst for the reaction CO₂ with H₂O must possess: (i) the ability to excite valence electrons with visible light, (ii) a high activity/selectivity toward CH₃OH and hydrocarbons, and (iii) catalyst stability. No catalyst has been identified that exhibits both promising activity and stability during photosynthesis of CO₂ and H₂O to form CH₃OH or CH₄. 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 this project (DE-FG26-99FT40579), we have carried out catalyst screening study using the full range of light. The preliminary results of this study paved the way to propose a series of experiments to develop a fundamental understanding of photocatalysis of CO₂ conversion. 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.

EXECUTIVE SUMMARY

This innovative research project aims at determining the feasibility of using TiO₂-based catalysts for photo-catalytic conversion of CO₂/H₂O to methane and methanol. The key research efforts focused on (i) setting up a photocatalytic reactor system, (ii) preparation of 0.5 wt% Rh/TiO₂, 0.5 wt% Pt/TiO₂, TiO₂, 0.5 wt% Cu/TiO₂, Ti silsesquioxane, and 0.5 wt% Cu/SrTiO₃, (iii) testing photo-catalytic activity and selectivity, and (iv) development of novel concept of photo-synthesis. 0.5 wt% Cu/SrTiO₃ was found to be the most active and selective catalyst for methanol synthesis. This catalyst will be used for in situ IR study in the Phase II research project for determining the mechanisms of methanol synthesis from CO₂/H₂O. Identification of active adsorbates and sites will allow incorporation of acid/basic sites to alter the nature of CO₂ and H₂O adsorbates and with Pt/Rh/Cu sites to direct reaction pathways of surface intermediates, enhancing the overall activity and selectivity for methanol and hydrocarbon synthesis.

EXPERIMENTAL

Catalyst Preparation

0.5 wt% Rh/TiO₂, 0.5 wt% Pt/TiO₂, TiO₂, 0.5 wt% Cu/TiO₂, and 0.5 wt% Cu/SrTiO₃ were all 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. The exceptions to this were the Cu-based catalysts, which were only calcined and not reduced. The Ti silsesquioxane Ti(O-iPr){(c-C₅H₅)₇Si₇O₁₂} was obtained from Mark Crocker of the Shell Oil Company.

Slurry Reactor

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 carry out catalyst screening. Each reaction run employed 10 ml H₂O, 15 ml CO₂, and 500 mg catalyst. The CO₂ 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 for different duration of time. The liquid products were sampled and analyzed via GC (HP 5890A with 80/100 PORAPAK-Q column) to determine the hydrocarbon composition.

RESULTS AND DISCUSSION

Basic Theory

Figure 2 illustrates the general scheme of the photocatalytic process on a solid catalyst (6). The first step of the process is the generation of electron-hole pairs in the semiconductor particle. The electron-hole pairs are produced by excitation of electrons from the valence band to the conduction band by light absorption with an energy equal to or greater than the band gap of the semi-conductor (shown in the inset). Upon excitation, the separated electrons and holes can follow several pathways: (I) surface recombination, (II) recombination in the bulk, (III) donation of the electron to an electron acceptor (A) adsorbed on the surface, and (IV) a hole may migrate to the surface and accept an electron from a donor species on the surface. The species A^- and D^+ may further react to yield products. The efficiency of the process depends on the effectiveness of the catalyst surface to transfer electrons from/to adsorbed species. Unfortunately, no information/knowledge exists regarding the electron transfer mechanism or an approach for enhancing it.

It is generally recognized that the ability of a semiconductor to undergo photo-induced electron transfer to/from adsorbates (i.e., A and D in Fig. 1) is governed by the band energy positions of the semiconductor and the redox potentials of the adsorbates. Figure 3 illustrates the band edge positions of several semiconductors and the redox potential of the following two reactions that take place on the catalyst surface (10-13).

The potential level represents a driving force for electron transfer between adsorbates and semiconductors. The potential level of the donor, such as H_2O , needs to be above (more

negative than) the valence band position of the semiconductor in order to donate an electron to the vacant hole. The potential level of the acceptor, such as CO₂, is required to be below (more positive than) the conduction band potential of the semiconductor. It is important to note that the band gaps included in Fig. 3 are the band gaps of the bulk material. Due to the lack of surface band gap data and a failure to recognize the significant difference between the bulk and surface band gaps, bulk band gap data have often been used to select photocatalytic materials. Results of these studies did not usually provide information that could be used for elucidation of the reaction mechanism or further catalyst development.

The key mechanistic issues to be addressed are (i) the knowledge of the surface band gap and its relation to the surface structure and (ii) the reactivity of adsorbates and their reaction pathways. The importance in identifying active adsorbates and determining their reactivities should not be underestimated. The structure of adsorbates is also closely related to the state of the sites to which adsorbates bind. Determination of the reactivity and structure of adsorbates provides essential information for elucidation of the nature of active sites and for development of a scientific basis for catalyst design.

Reaction Results

Our initial study was motivated by (i) a lack of an experimental approach to determine the reactivity of adsorbates during photosynthesis reactions and (ii) an absence of photocatalytic syntheses beyond using UV radiation at ambient conditions. Our major effort focused on catalyst screening. Table 2 lists the rate of product formation of the photocatalytic reaction of CO₂/H₂O that was carried out with a mixture of catalyst and liquid water in a batch reactor at 298 K. Ti silsesquioxane [Ti(O-iPr){c-C₅H₅}₇SiO₁₂] exhibited excellent activity for CH₃OH. This interesting property may be related to its unique structure. The Cu/SrTiO₃ also exhibited

comparable activity. The activity of the catalysts for methanol synthesis decreased in the order: Ti silsesquioxane > Cu/SrTiO₃ > Pt/TiO₂ > Cu/TiO₂ > TiO₂ > Rh/TiO₂. Since the surface area of the TiO₂ catalyst used in this study is in the range of 30-40 m²/g, it would be beneficial to increase its surface area to accommodate the more active sites for the reaction. We propose to prepare monolayer and multi-layer TiO₂ on the high surface mesoporous material. These high surface area mesoporous materials usually have a surface area of more than 800 m²/g. Increasing the TiO₂ surface area from 40 m²/g to 800 m²/g may lead to a 20-folds increase in the activity of the catalyst.

Future research

A number of characteristics are required for a photocatalyst to be effective for methanol synthesis. This is revealed upon examination of the redox reactions of H₂O and CO₂:

1. The surface band gap of the catalyst must be greater than the difference in the reduction potentials of the reactants' redox reactions (i.e., CO₂ and H₂O).
2. The catalyst surface must provide sites for both H₂O and CO₂ adsorption.
3. The catalytic site should allow facile transfer of electrons to and from adsorbates and minimize electron-pair recombination both at the surface and in the bulk.
4. The catalyst surface should allow proton generated at the H₂O site to migrate to the CO₂ site, or conversely, to initiate the conversion of CO₂ to methanol.

Development of an effective catalyst which possesses these characteristics 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.

Catalyst Preparation.

Al-MCM-41-based catalysts will be prepared by ion exchange of Na-containing Al-MCM-41 using Ti, Cd, and Zn, acetate. Cu, Pt, and Rh sites could be added to provide the sites for adsorption of CO₂ and formation of methanol or hydrocarbons. These metals can modify the surface properties of TiO_x, CdS, and ZnS.

Highly dispersed and monolayer Ti, Cd, and Zn oxide/sulfide will be prepared by grafting metal precursors, including Ti(OCH₃)₄, Cd(acac)₂, (acac = (CH₃COCH=C(O⁻)CH₃)), and Zn(C₂H₅O₂)₂ on the surface of Al₂O₃ and Al-MCM-41. Due to the uncertainty in the long-term hydrothermal stability of these monolayer oxides and sulfides/Al-MCM-41, a post-synthesis treatment will be used to deposit Ti, Cd, and Zn oxide layers. Prior to grafting, Al₂O₃ and Al-MCM-41 (Al/Si ratio=30) will be thermally pretreated to remove physisorbed H₂O, leaving OH on the surface. It should be noted that both thermally treated Al₂O₃/Al-MCM-41 and the metal methoxide precursors are moisture and air sensitive; their preparation will be conducted in a dry box. Ti, Cd, and Zn precursors will be bought in contact with Al₂O₃ or Al-MCM-41 by using a hexane or pentane solution at 300 K. The concentration of metal precursors can be carefully controlled to avoid dimer or trimer formation before grafting. The use of a non-polar solvent minimizes the interface and enhances the interaction between the metal precursor and the surface OH groups.

To understand the nature of the grafting reaction and determine the optimum thermal treatment and grafting condition, the monolayer oxide preparation process will be examined by in situ IR. Al_2O_3 and Al-MCM-41 will be pressed in the form of a thin disk and placed in the in situ IR cell to undergo thermal treatment. The metal precursor solution will be injected to the IR cell to contact the Al_2O_3 /Al-MCM-41 disk at 300 K. IR spectroscopy will (i) determine the relative density of OH groups (number/area) on the Al_2O_3 and Al-MCM-41 surfaces and (ii) insure the removal of H_2O prior to grafting. The grafting reaction between the metal precursor and various types of surface OH groups will be monitored as a function of temperature by infrared spectroscopy.

Since the spacing between two neighboring OH groups on a H_2O -free oxide surface is about 3.4 Å (14,15), the bulky size of $\text{Cd}(\text{acac})_2$ [10.67 Å x 5.36 Å x 5.00 Å] will not be able to react with all OH groups on the surface. The catalysts prepared from these bulk precursors may contain highly dispersed, individual cations on the surface of Al_2O_3 and Al-MCM-41. Repeated grafting is needed to achieve the monolayer of grafted oxide. The small size of metal methoxide [4.1 Å x 2.8 Å] should be able to react with all surface OH groups. Since Al sites on Al-MCM-41 have higher acidity than Si sites, they may preferentially react with OH on Al sites. The monolayer oxide on Al-MCM-41 is expected to be hydrothermally stable. McCullen and Vartuli have found that the post synthesis treatment of as-synthesized MCM-41 with metal alkoxide results in the formation of metal oxide layer, giving excellent hydrothermal stability up to 973 K with 100% steam (16).

Al-MCM-41 can be prepared by mixing solution A [Tetramethyl ammonium hydroxide, Cab-O-Sil silica, and H_2O] with solution B [NaAlO_2 , cetyltrimethylammonium chloride (CTMACl), NaOH, N,N-dimethylhexadecylamine (DMHA), and H_2O]. DMHA is found to be

an effective expander. The use of the DMHA/CTMACl ratio of 1, results in the large pore (7.7 nm) MCM-41 (20). The mixture will be heated in an autoclave under autogenous pressure at 363 K for 48 hours. Part of the resulting gel will be calcined at 773 K for grafting metal precursors; part of gel (as-synthesized Al-MCM-41) will be further mixed with Ti precursor solution to initiate the stabilization reaction as described by McCullen and Vartuli (16):

Si-O-R denotes the state of as-synthesized Al-MCM-41 containing R, such as CTMA⁺, prior to calcination. The resulting sample after calcination at 773 K will yield Zn, Ti, and Cd-containing Al-MCM-41. The grafting or stabilization reaction may be an effective approach to provide long-term hydrothermal stability as well as unique catalyst activity for photocatalytic synthesis of CH₃OH and hydrocarbons.

Multilayer Ti oxide will be prepared by repeating the grafting process with metal methoxide precursors, calcinations, exposure to H₂O, thermal treatment to control OH surface density to build oxide layers on Al₂O₃ and Al-MCM-41 surface. The SrTiO₃ layer can be prepared by deposition of layer of Sr[OOCCH₃]₂ on Ti oxide layer and followed by calcination.

Our studies have shown that Pt and Cu may provide the site for the formation of methanol and hydrocarbons, from intermediates produced by the photocatalytic reaction of CO₂/H₂O over oxide and sulfide layer surfaces. It is important to provide these sites on the surface of Zn, Ti, and Cd oxide and sulfide layers to increase the selectivity of the reaction. To further modify the acid/base properties of the surface of these monolayer oxides. Al(CH₃)₃ (17) and/or AlCl₃ can be used as a precursor to deposit acid sites while La[OCH(CH₃)₂]₃ can be used to decorate basic sites on the surface of monolayer oxides. The exposure of the catalyst sample to a very dilute precursor stream may decorate the oxide surface with these components, whereby

calcination would lead to the formation of discrete Al_2O_3 moieties (18) either on or within the monolayer oxide. To avoid interaction of Al precursors with Cu, Pt, and Rh sites, these surface sites may be protected by pre-adsorbing CO prior to grafting. The decoration of the monolayer oxide surface with sites of adjustable acid/basic strength and the sites for enhancing CH_3OH /hydrocarbon selectivity may allow optimization of adsorption of $\text{H}_2\text{O}/\text{CO}_2$ and selectivity of photocatalytic synthesis of CH_3OH and hydrocarbons.

In Situ IR Study

The dynamic reactivity of adsorbates for the $\text{CO}_2\text{-H}_2\text{O}$ reaction will be studied with the in situ IR cell using a Hg lamp and a set of interference filters to provide a specific energy range of photons. The energy density of the photon beam will be measured with a photomultiplier tube photodiode (PMT) detector and calibrated with a photo-thermopile detector. The catalyst surface (i.e., adsorbate population and type) and effluent gas phase composition will be monitored via IR and MS, respectively. A known amount of $^{13}\text{CO}_2$ and D_2O will be injected to trace the reaction pathway of ^{13}C - and D-containing species. The response of ^{13}C - and D-containing adsorbates and final products may allow elucidation of the rate-limiting step. The reaction pressure and temperature will be varied to optimize the formation of products. Results of our preliminary study have shown that increasing the reaction temperature and CO_2 pressure dramatically increased the hydrocarbon formation rate.

Probing the Reactivity and Reaction Pathways of Adsorbed Intermediates

A number of probe molecules such as HCOOH and CH_3OH will be adsorbed onto the catalyst to study their reactivity and reaction pathway through monitoring the transient IR response of these adsorbed probe molecules as well as their subsequent products. The probe

molecule approach may serve as a complement to the in situ IR isotopic transient technique for determining the reactivity of those species, which give a low IR absorbance intensity.

Catalyst Characterization

The composition of these catalysts will be verified by X-ray fluorescence spectrometry using a Philips PV 9550. The structure of Al-MCM-41 and $\text{Al}_2\text{O}_3/\text{Al-MCM-41}$ -supported monolayer catalysts: Ti oxide, ZnS, or CdS will be determined by small angle X-ray scattering (SAXS). The surface area of all materials will be measured by the BET method. Finally, the acidity of the catalyst will be determined by infrared spectroscopy combined with a NH_3 temperature-programmed desorption.

X-ray absorption spectroscopy, including absorption edge measurement (XANES) and extended X-ray fine structure (EXAFS) will be carried out at either X-18B or X-19A beamline of the National Synchrotron Light Source at the Brookhaven National Laboratory. The spectra for the catalysts before and after reaction studies will be measured at room temperature. The X-ray data are expected to provide information about the coordination numbers and metal-oxygen distance. The method of data analysis and reduction will follow those reported in Koningsberger and Prins (19). The structure information obtained will verify whether oxide and sulfide monolayers are achieved on the catalysts (prepared by grafting) and will allow elucidating the coordination environment of these sites.

The surface band gap of the catalyst will be measured by scanning tunneling microscopy (STM). The sample will be placed on the sample stage and subjected to electronic bias. The tunneling current will be measured as a function of bias. The band gap can be determined from the difference in biases, which yield positive and negative currents.

CONCLUSION

The long-term goal of our research has been to develop a fundamental understanding of the reactivity of adsorbates and their relationships with the nature of sites, reaction kinetics, and deactivation resistance. 0.5 wt% Cu/SrTiO₃ was found to be the most active and selective catalyst for methanol synthesis. The activity of the catalyst decreased in the order: Ti silsesquioxane > Cu/SrTiO₃ > Pt/TiO₂ > Cu/TiO₂ > TiO₂ > Rh/TiO₂. To further increase the number of site for the reaction, we propose to prepare monolayer and multiplayer TiO_x on high surface area mesoporous oxides. Preparation of supported monolayer oxides and sulfide catalysts with metal sites and acid/base functionality as well as investigation of their structures and catalytic properties constitutes an important and innovative element of next phase study. The unique coordination of these monolayer sites and their chemical environments promises to open opportunity for development of new types of photocatalysis for methanol and hydrocarbon synthesis from CO₂ and H₂O.

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Fig. 1. Experimental apparatus

Fig. 2. Pathways of electron/ hole pairs and A and D adsorbates.

Fig. 3. Band energies for various semiconductor and CO₂/H₂O reduction potential.

Table 1. CO₂ migration options

CO ₂ Migration option	Reduction Potential (Million Tons of CO ₂)	Net Cost (1990 \$) (\$/ton CO ₂ avoided)	
<i>CO₂ capture and sequestration technologies</i>			
		High	Low
Capture with utilization	20	5	0
Capture with enhanced oil recovery	50	45	10
Capture with geological storage	900	91	31
Capture with ocean storage	600	91	31
<i>Energy supply technologies</i>			
		High	Low
Nuclear	1500	61	13
Hydroelectric	30	38	25
Biomass	130	42	8
Geothermal	69-235	144	0
Wind	30	125	0
Solar photovoltaic	400	400	23
Solar thermal	540	178	24
<i>“Least-regrets” options</i>			
		High	Low
Energy efficiency	425-620	6	-
Supply efficiency	99	2	0
Fuel switching to gas	850	46	17
Forestation	242	10	3

Table 2. Photosynthesis of Hydrocarbons and Methanol from CO₂/H₂O

Catalyst	Gas-Phase Product	Liquid-Phase Product	Initial Rate C₁ HC ($\mu\text{mol/hr/g}_{\text{cat}}$)	Initial Rate C₂₊ HC ($\mu\text{mol/hr/g}_{\text{cat}}$)	Final Rate C₁ HC ($\mu\text{mol/hr/g}_{\text{cat}}$)	Final Rate C₂₊ HC ($\mu\text{mol/hr/g}_{\text{cat}}$)	Avg. Rate MeOH ($\mu\text{mol/hr/g}_{\text{cat}}$)
0.5 wt% Rh/TiO ₂	C ₁ -C ₂	MeOH	.73	.12	.02	--	24.0
0.5 wt% Pt/TiO ₂	C ₁ -C ₂	MeOH	1.1	.54	--	--	85.8
TiO ₂	C ₁	MeOH	--	--	.01	--	47.5
0.5 wt% Cu/TiO ₂	C ₁ -C ₃	MeOH	.09	.42	.002	-.004	80.0
Ti silsesquioxane	C ₁ -C ₅	MeOH	1.12	2.38	.002	.1	145.6
0.5 wt% Cu/SrTiO ₃	C ₁ -C ₂	MeOH	.15	.32	--	--	135.8

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 H₂O (l), 20 mL CO₂ (g), 500 mg cat., 298 K, 0.1 MPa.