

PHOTOCATALYTIC CONVERSION OF CO₂ – AN ALTERNATE TO STORAGE BASED SEQUESTRATION

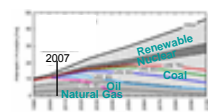


Introduction

The incentive for photocatalytic reduction of CO₂ comes from the need to reduce CO₂ in environment.

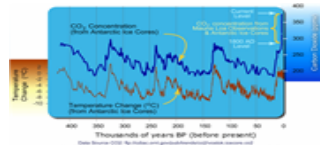
- Global CO₂ Emissions - 24,126,416 thousand metric tons
- US CO₂ Emissions - 5,872,278 thousand metric tons

Primary Sources of Atmospheric CO₂



- Biological Sources "Natural Carbon Cycles"
- Anthropogenic Sources
 - Combustion of Fossil Fuels for Energy
 - Waste Combustion
 - Chemical/Material Production and Manufacturing

Global Effects of Anthropogenic CO₂



2004 CO₂ emission show a 47.5% increase in 1980 emission values

Energy Information Administration/ International Energy Annual 2004

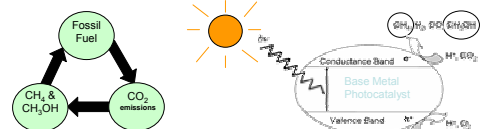
Current Methods for CO₂ Sequestration

- CO₂ Capture – Aqueous Amines
 - ~30% aqueous amines can attain a loading of .5 mol/mol of amine
- CO₂ Storage - gradient approximation (PW91 functional)

GE and BP have announced a joint venture to produce hydrogen from fossil fuels. 90% of CO₂ will be captured and injected into deep geological formations.

Alternatives to CO₂ Sequestration

Recycle CO₂ Photocatalytic process



State-of-the-art: TiO₂

Several Approaches to Enhance CO₂ Conversion

- 100% Gas Phase Reaction
 - Eliminates competing reactions and solubility limitations
- Quantum Size Effect
 - Highly dispersed TiO₂ enhances optical and chemical properties
- Tetrahedral Titanium Coordination Environment
 - Increases activity and methanol selectivity
 - These conclusions are not necessarily true because multiple variables have been changed in these studies
 - pore size, surface area, morphology and preparation methods
 - Chemistry might be taking place in confined area since the catalyst is in silica matrix in Ti incorporated silica molecular sieves

TiO₂ is not an ideal Catalyst...

- TiO₂ catalysts exhibit low turnover frequency for CO₂ conversion to organic molecules
- TiO₂ absorbs in the UV region - a narrow range of solar spectrum
- 96% of the solar spectrum is in the visible region

Catalyst	g _{cat} /g _{cat}	TOF ^a	CH ₃ OH Sel. ^b	Production of 100 mL CH ₃ OH / hour		
				mol CO ₂	container (l ³)	g of cat.
Ti-MCM-48	9.96e ⁻³	0.11	28.79%	8.58	53.30	81.04
Ti-SBA-15	2.95e ⁻³	0.39	20.72%	11.92	74.06	30.22
Ti-PS (c. 50) thin film	1.59e ⁻²	0.05	59.04%	4.18	25.99	89.59

a) Moles of CO₂/h converted to methanol and methane per gram of catalyst.
b) Selectivity assumes the CO₂ is only converted to methanol and methane.
c) Container required assuming 1CO₂: 5 H₂O and 50°C.

Our Approach

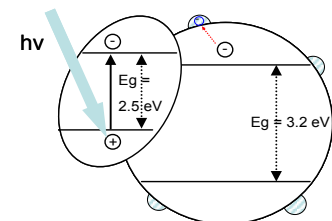
Reinvestigate TiO₂ based catalysts

- Octahedrally coordinated Ti impregnated on SiO₂
 - dispersed TiO₂ anatase phase nanoparticles
- Octahedral coordination but better distribution of TiO₂ in SiO₂ matrix
 - decomposition of [RO]₂Si-O-Ti[OR]₃ maintains Si-O-Ti
- Maintain Si/Ti but change Ti coordination (octahedral and tetrahedral) (thermal treatment)
 - titanium incorporated mesoporous silica
- Maintain tetrahedral coordination but lower the Si/Ti ratio
 - titanium incorporated mesoporous silica

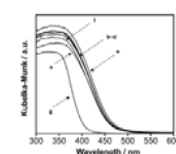
New catalysts:

The new catalysts needs to incorporate following properties:

- Shift Absorption to Visible
- Employ Charge Carrier Traps



Ru/(Ga_{1-x}Zn_x)(N_{1-x}O_x) absorbs in visible light and its thermal treatment has been shown to have an impact on its UV-Visible spectrum.



The UV-visible diffuse reflectance spectra of (Ga_{1-x}Zn_x)(N_{1-x}O_x) after various thermal treatments (a) fresh (b) 200 (c) 500 (d) 600 (e) 700 (f) 800 (g) 900 °C.

High temperature treatment not only reduces the number of catalyst sites but also induces a slight red shift, however, a blue shift occurs after thermal treatment at 900C primarily due to collapse to (Ga_{1-x}Zn_x)(N_{1-x}O_x).
Maeda, K. et al.; J. Catal. 254 (2008) 198.

Experimental

Synthesis

Synthesis of tetrahedral Ti in a SiO₂ matrix

A 100 mL Shlenk flask was charged with ethanol (42 mL), concentrated HCl (1.6 mL) and F108 (EO₁₃₀PO₆₀EO₁₃₀, BASF (5.4 g). Commercial Ti(tetraethoxide) (2 mL) was added to the reaction mixture with stirring. A solution TEOS (10 g, 10.75 mL) and 0.1M HCl (6.7 mL) was added to the reaction mixture while stirring. The reaction mixture was stirred for 4.5h and dried slowly in a petri dish to obtain a clear yellow gel. The gel was pyrolyzed at 350°C (rate 1°C/min, hold 3h) followed by calcination at 600°C (rate 1°C/min, hold 5h) to obtain 4.5 g of the mixed mesoporous metal oxide as a white powder.
[Shu, H. et al.; J. Phys. Chem. B, 108 (2004) 20038].

Synthesis of ZnGa₂O₄:

Commercial alkoxides were used as received. A 100 mL Shlenk flask was charged with Ga(OPr)₃ (1.77 g, 5.78 mmol) and 25 mL methoxyethanol solution of Zn(OCH₂CH₂OCH₃)₂ (1.25 g, 5.78 mmol). The reaction mixture was stirred on a magnetic stirrer and H₂O (0.52 g, 28.9 mmol) dissolved in methoxyethanol. A gel immediately formed which was dried and the free-flowing powder was pyrolyzed at 400°C to obtain 2.0 g of ZnGa₂O₄ powder.

Synthesis of RuO₂/(Ga_{1-x}Zn_x)(N_{1-x}O_x)

Nitridation of ZnGa₂O₄ powder was carried out under 100 mL/min flow of 1.5% NH₃ at 850°C for 10h and resulted in a yellow powder. Dispersion of RuO₂ (5 wt% Ru) on the GaN:ZnO powder achieved through impregnation of the powder with Ru₃(CO)₁₂ in a THF solution. After removal of THF and oxidation in static air at 350°C/1h a green powder was obtained.

Photocatalytic Activity Measurements

A 3-dimensional u-shaped cylindrical quartz tube closed to the atmosphere by Teflon stopcocks was used as a 67 mL capacity photoreactor vessel. A tubular 400W Hg lamp was placed in the open center of the reactor vessel. The catalyst sample (0.10g) was placed within the enclosed portion of the reaction vessel at the same height as the illumination from the Hg-lamp. Glass beads were placed on either side of the catalyst to prevent loss while the vessel is under vacuum for removal atmospheric air. After the air has been flushed from the vessel by vacuum/nitrogen cycling, the vessel was put under a complete CO₂ atmosphere and 1mL of deionized H₂O was added to it. The closed vessel was then placed in a circulating water bath and heated to 50°C. The photoreactor vessel was illuminated for 380 mins before the gas content was evaluated by GC-MS via syringe sampling.

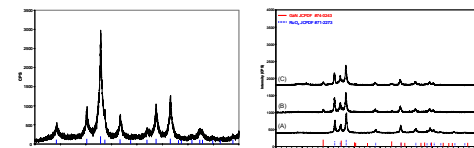


Results & Discussion

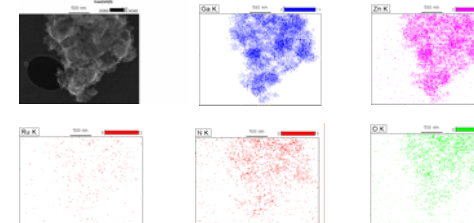
We initiated our studies by reinvestigating CO₂ photocatalytic reduction employing TiO₂-SiO₂ catalyst which we synthesized by careful synthesis of Ti incorporated mesoporous SiO₂ monolith to contain a low Si/Ti ratio (5.5) with the Ti⁴⁺ atoms in tetrahedral coordination. When 0.5 g of this catalyst was exposed to UV light for 8hrs in the presence of CO₂ (360 μmol) and H₂O (30 μL), methanol was found in the product stream which was confirmed by GC-MS. This catalyst did not appear to be a very promising candidate for modification.

Our focus has been primarily on (Ga_{1-x}Zn_x)(N_{1-x}O_x) which has been shown to be an effective catalyst for photocatalytic hydrogen generation from water.

The literature synthetic method for this catalyst involves heating a mixture of Ga₂O₃ and ZnO₂ in an ammonia atmosphere. We synthesized this material employing modern synthetic chemistry. The hydrolysis of Ga(OR)₃ and Zn(RO)₂ leads to a gel which furnishes pure ZnGa₂O₄ upon pyrolysis. The XRD of the sample shows single phase material. Nitridation and subsequent impregnation furnishes Ru/(Ga_{1-x}Zn_x)(N_{1-x}O_x). The XRD of this material shows peaks for GaN and Ru which are expected for this catalyst.



XRD of ZnGa₂O₄ prepared by solution methods from alkoxides calcined at 400°C. Diffraction line reference is ZnGa₂O₄ JCPDF #71-0843.
XRD of GaN:ZnO solid solution (A) as-prepared by nitridation (B) fresh impregnated with RuO₂ (C) photocatalytically tested RuO₂/(Ga_{1-x}Zn_x)(N_{1-x}O_x).



The SEM of the catalyst exhibits agglomerates of 500nm+ particles. The electron mapping suggests a homogenous distribution of Ga, Zn, and Ru in the catalyst.

The UV photocatalytic CO₂ reduction on this catalyst produces CO rather than methanol at a rate of 43.3 nmols in 380 min.

Conclusions

- Reinvestigation of Titanium based catalyst suggests that it is not a highly effective photocatalyst for CO₂ reduction.
- Ru/(Ga_{1-x}Zn_x)(N_{1-x}O_x) can be synthesized by modern synthetic techniques resulting into a homogeneous distribution of Ga and Zn in the catalyst.
- Photocatalytic reduction of CO₂ on this new catalyst produces CO with high selectivity.
- Since this catalyst is known to produce hydrogen from water under visible radiation, we propose a synthetic gas production cell from CO₂ and water. This synthetic gas can be converted to a variety of organics by traditional Fisher-Tropsch routes.

Publications

- Debusk, M.M.; Narula, C.K.; Chemical routes to photocatalysts: nanosizing Ru/GaN:ZnO, American Chemical Society National Meeting, Salt Lake City, Utah March 2009.
- DeBusk, M.M.; Narula, C.K.; Energy & Environmental Science (invited) (manuscript in preparation).

Acknowledgement

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