SOUTHWEST CATALYSIS SOCIETY (SWCS)

2008 SPRING SYMPOSIUM

April 4, 2008

Farnsworth Pavilion
<u>Rice University</u>
Houston, TX

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Greetings!

The 2008 SWCS Spring Symposium will be held on **Friday, April 4, 2008**, at Rice University, Houston, TX.

Rice University is roughly 25 miles from George Bush Intercontinental Airport and 18 miles from Hobby Airport. The symposium is to be held at the Farnsworth Pavilion located in the Ley Student Center/Rice Memorial/Chapel building (http://www.rice.edu/maps/). Detailed driving directions and maps can be obtained from http://www.rice.edu/maps/directions.html/. (blue = linked to web page)

On-site registration will begin at 7:45 AM and the program will begin at 8:15 AM. The list of podium speakers and poster presentations is given below. There will be coffee/beverages provided throughout the day and food will be available to purchase during lunch break.

The 2008 Spring Symposium **registration fee is $40**, which includes membership dues. For those who cannot attend the Symposium, please mail in your membership due ($25) to our Treasurer, George Stanley (mailing address shown at left). You also automatically become members of the North American Catalysis Society for one year. **Students pay $15** for registration (membership due included). Group registration can be accommodated on-site; the group representative is to bring a list of names and email addresses and appropriate total registration fee.

There will also be a poster session at the Symposium. For meritorious posters, we will offer **Best Poster awards**, carrying a cash prize of $200-300 each. We encourage students and postdocs to submit abstracts for poster presentations to Dr. Yun-feng Chang (yun-feng.chang@exxonmobil.com). The deadline for poster abstract submissions is this Friday, March 21.

We look forward to see you at the meeting.

Sincerely,

Yun-feng Chang   Michael Wong
Chair   Chair-Elect

PROGRAM

7:45 AM   **Registration- George Stanley (Louisiana State U., Baton Rouge, LA)**
Farnsworth Pavilion, Rice University, Houston, TX

8:15 AM   **Yun-feng Chang – Chair (ExxonMobil Chemical, Baytown, TX)**
Welcoming Remarks
Mike Wong – Chair-Elect (Rice U., Houston, TX)
Opening of 2008 SWCS Spring Symposium

8:30 AM   **Dr. Bob Farrauto – Ciapetta Lecturer (BASF, Iselin, NJ**)
Ciapetta Lecture: Combining Industrial and Fundamental Research for
Commercial Success

9:15 AM   **Robert Clayton, Ashok Kumar, Jin Xu, <u>Michael P. Harold</u>, Vemuri Balakotaiah, (University of Houston, TX**)
Spatio-Temporal Behavior of NOx Storage and Reduction Monolith Catalysts

9:45 AM   **Coffee Break (sponsored by Crystaphase Products, Micromeritics)**

10:05 AM   **Gary Gildert (Custom Catalytic Solution Inc., La Porte, TX)**
The Seven Steps to Specifying a Hydrogenation Catalyst Bed

10:35 AM   **Daniel F. Shantz (Texas A&M U., College Station, TX)**
Understanding the Interplay between Dynamics and Reactivity of Organic Layers
Deposited on MCM-41

11:05 AM   **<u>L. Burns</u>, G. Anderson, S. Eijsbouts, S. Mayo, K. Riley (Albemarle, Pasadena, TX)**
Dimensions in Catalyst Design: FCC Feed Hydrotreating Catalysis

11:35 AM   **Lunch Break/Poster Preview**

1:00 PM   **Zachary T. Ball (Rice U., Houston, TX)**
Copper Complexes for Carbon-Silicon Bond Activation: Access to Organocopper
Reagents from Stable Organosilane Precursors

1:30 PM   **<u>Karen Martirosyan</u> and D. Luss (University of Houston, Houston, TX)**
Development of Ce-Zr Nano-oxide Catalysts for Diesel Particulate Filters

2:00 PM   **Poster Session (sponsored by ExxonMobil, SABIC, ChevronPhillips)**
Coffee Break (sponsored by Hiden Analytical Inc. , SASOL North America)

1. **Divesh Bhatia, Michael P. Harold and Vemuri Balakotaiah (U. of Houston, Houston, TX)**

Global Kinetics for NO Reduction and CO & H_2 Oxidation in Monolith Reactors

2. **Yun Cai, Feng Gao, Kerrie Gath, D. Wayne Goodman (Texas A&M U., College Station, TX)**

In Situ Investigations of CO Oxidation on Pt-Group Metal Catalysts: From Ultrahigh Vacuum to Elevated Pressures

3. **Robert D. Clayton, V. Balakotaiah and M. P. Harold (U. of Houston, Houston, TX)**

NOx Storage and Reduction with H_2 on Pt/BaO/Al_2O_3 Monolith: Spatio Temporal Resolution of Product Distribution

4. **Freddy Avila Diaz and Kerry Dooley (Louisiana State U., Baton Rouge, LA)**

Ketonization - Catalyst Comparisons With and Without Water in Feeds

5. **Yu-Lun Fang, Kimberly N. Heck, Xianhuai Huang, Qilin Li, Pedro J. J. Alvarez and Michael S. Wong (Rice U., Houston, TX)**

Immobilization and Testing of Pd-on-Au Nanoparticles for Catalyzed Trichloroethene Hydrodechlorination in Water

6. **Kerrie K. Gath, F. Gao, M.S. Chen, Y. Cai, and D.W. Goodman (Texas A&M U, College Station, TX)**

Reactivity of CO on Oxygen-Saturated Rh and Pd Surfacee: An X-Ray Photoelectron Spectroscopic Study

7. **Kimberly N. Heck, Naomi J. Halas, Michael S. Wong (Rice U., Houston, TX)**

In-situ Monitoring of Catalyzed Aqueous-Phase Trichloroethylene Hydrodechlorination using Pd-on-Au Nanoshells via Surface-Enhanced Raman Spectroscopy

8. **Sameer H. Israni and Michael P. Harold (U. of Houston, Houston, TX)**

Generation of High Purity Hydrogen from Ammonia Decomposition using Nanopore Palladium Membrane Based Catalytic Reactors

9. **Saurabh Y. Joshi, Michael P. Harold, Vemuri Balakotaiah (U. of Houston, Houston, TX)**

Low-Dimensional Models for Real Time Simulations of Catalytic Monoliths

10. **Vikram Kalakota and Kerry Dooley (Louisiana State U., Baton Rouge, LA)**

Removal of H_2S using Regenerable Sorbents of Rare Earth/Transition Metal Oxides

11. **Ashok Kumar, V. Balakotaiah, Michael P. Harold (U. of Houston, Houston, TX)**
TAP Studies of NO_X Storage and Reduction on Variable Dispersion $Pt/BaO/Al_2O_3$ Catalysts

12. **Zengcai Liu, Daxiang Huang, Shirlaine Koh, Chengfei Yu , K.L. More, L. F. Allard Jr., Peter Strasser (U of Houston, Houston, TX)**
Stabilized and Enhanced $PtCu_3/C$ oxygen Reduction Electrocatalysts via Au Galvanic Displacement

13. **Morgan Reed, Joe Hutchins, Eric Peterson, Dan Rutman, Eddie Gaston, Jewel Gomes and David Cocke (Lamar U., Beaumont, TX)**
Mechanochemical Synthesis of Novel Nanoparticle Catalyst

14. **Ratndeep Srivastava, Prasanna Mani, and Peter Strasser (U of Houston, Houston, TX)**
$Pt-M$ and $Pt-M_1-M_2$ core-shell electrocatalysts for oxygen reduction reaction in PEMFC

15. **Fan Yang, M. S. Chen and D. W. Goodman (Texas A&M U., College Station, TX)**
Scanning Tunneling Microscopy for Model Catalytic Studies

16. **Jin Xu (U. of Houston, Houston, TX)**
Modeling of Catalytic NO Reduction by H_2 and NH_3 in O_2 on Pt/Al_2O_3

17. **Xiaobing Zhu, Ratndeep Srivastava, Shirlaine Koh, Zengcai Liu, Chengfei Yu, and Peter Strasser (U of Houston, Houston, TX)**
Carbon Support Effects on Oxygen Reduction Fuel Cell Electrocatalysts by Voltammetric Surface Dealloying

3:30 PM **Awards & Recognitions**

3:40 PM **Adjourn**

Combining Industrial and Fundamental Research for Commercial Success

(2008 Ciapetta Lecture)

Robert. J. Farrauto

BASF Catalysts, 101 Wood Avenue Iselin, NJ 08830, USA

Adjunct Professor Columbia University, New York City
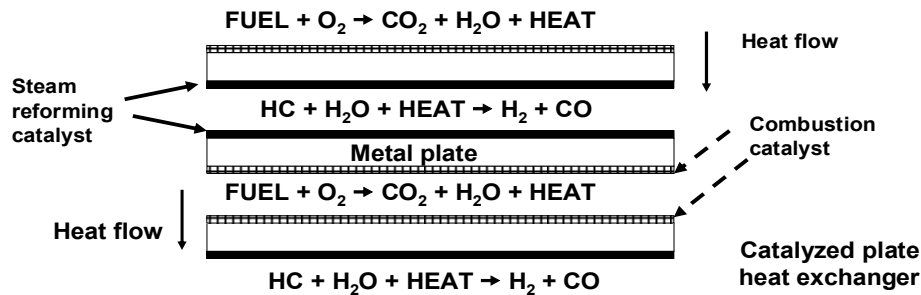
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Abstract

Distributed hydrogen for the hydrogen economy will require new catalysts and processes. Existing large scale hydrocarbon steam reforming plants can not simply be reduced in size to meet the size, economic, safety, and frequent duty cycle requirements for applications for fuel cells, hydrogen fueling stations, and industrial uses such as hydrogenation reactions, gas turbine cooling, metal processing, etc. Consequently, there is a need to completely reassess how hydrogen can be made for the emerging hydrogen economy.

Unlike the catalytic processes in the chemical and petroleum industries that operate at steady state conditions hydrocarbons reformers integrated to fuel cells must operate in a transient mode to follow the power load demand. As the power requirements rapidly change so must the rate of hydrogen delivery. Thus the process and catalyst materials must be designed for large turn-down-ratios especially with regard to space velocity and rapid transients in temperature. The nature of these operations must be factored into the catalyst and system design.

A key limitation of traditional base metal (Ni, Cu, Cr, Fe, etc) reforming particulate catalysts used in the chemical industry is their inability to sustain activity and mechanical stability after frequent start and stop tests. During these operations, common for processors integrated to fuel cells, the catalyst is rapidly heated and cooled causing mechanical failure of the catalyst particulate structure. During the cooling

process liquid water from the reformate stream condenses on the surface of the reduced catalyst causing it to oxidize and slowly deactivate. Reduced base metals spontaneously oxidize liberating large quantities of heat upon exposure to air generating rendering them unsafe for a consumer application such as a fuel cell.

Precious metal catalysts deposited on monolithic substrates are resistant to the deactivation modes experienced by base metals. They can be used without complicated and time consuming reductions required for base metal reforming catalysts. Precious metals are sufficiently robust that they can undergo start and stop modes without loss of activity after air or liquid water exposure. They are sufficiently active that only small amounts deposited on a monolith or heat exchanger wall can be used resulting in reformers with greatly reduced size and weight, lower pressure drop, enhanced mechanical stability, and rapid response to transient operations. For this reason hydrogen fueling stations are being built utilizing precious metal monolith technology (1). In the accompany figure a catalyzed plate heat exchanger is shown. The hydrocarbon-containing process gas is being steam reformed on the process side while the heat of reaction is provided by the catalytic oxidation of fuel and air on the combustion side. This design enhances heat transfer allowing for space velocities up to 10 times higher than traditional packed bed.

FUEL + O_2 → CO_2 + H_2O + HEAT

Heat flow

Steam reforming catalyst

HC + H_2O + HEAT → H_2 + CO

Metal plate

Combustion catalyst

FUEL + O_2 → CO_2 + H_2O + HEAT

Heat flow

HC + H_2O + HEAT → H_2 + CO

Catalyzed plate heat exchanger

Activity, selectivity and life testing must reflect the anticipated "duty cycle" the catalyst will experience during its lifetime. By combining realistic testing with fundamental research we have gained valuable insight into making improved catalysts and suggestions on process conditions to insure satisfactory performance.

Today's presentation will describe some of the technological successes we have achieved using precious metal catalysts on monoliths and catalyzed heat exchangers for reforming natural gas for the generation of distributed hydrogen.

(1) Farrauto, R., Liu, Y., Ruettinger, W., Ilinich, O., Shore, L. and Giroux, T. "Precious Metal Catalysts Supported on Ceramic and Metal Structures for the Hydrogen Economy" Catalysis Reviews 49, 411-496 (2007)

Biographical Sketch of Robert J. Farrauto

Dr. Farrauto is a Research Fellow at the Corporate Research Laboratories of BASF Catalysts (formerly Engelhard) in Iselin, New Jersey, USA. His major responsibilities have included the development of advanced automobile emission control catalysts and catalysts for the chemical industry. He managed an Engelhard research team that developed and commercialized diesel oxidation catalysts for the European, North American and Asian markets for passenger cars and heavy duty trucks.

Currently he manages a research team developing new catalyst technology for the hydrogen economy including hydrogen refueling stations and fuel cells for stationary, portable power and vehicular applications.

He is also Adjunct Professor in the Earth and Environmental Engineering Department of Columbia University, in the City of New York where he teaches course in catalysis.

Professional Activities

Co-author of *two books*

1) "Catalytic Air Pollution Control: Commercial Technology " second edition, Wiley and Sons, NY 2002

2) "Fundamentals of Industrial Catalytic Processes" second edition, Wiley and Sons, October 2005.

- Author/coauthor of 80 publications and 50 U.S. Patents.

Awards

1. ***Ciapetta Lectureship Award for 2008: The North American Catalysis Society***

2. Catalysis and Reaction Engineering Award from the AICHE (American Institute of Chemical Engineers)- 2005

3. Recipient of the Canadian Catalysis Foundation (Year 2000-2001) Cross-Canada lectureship Award

4. Recipient of the Henry Albert Award for excellence in precious metal catalysis in 2001 sponsored by the International Precious Metal Institute

5. Outstanding teaching Award from the New Jersey Institute of Technology 1995

6. Most cited author between 2001-2005 for paper entitled "Automobile Exhaust Catalysts" Applied Catalysis B: General (2001)

Education

- BS in Chemistry from Manhattan College (1964), New York City

- PhD. from Rensselaer Polytechnic Institute (1968), Troy, New York.

Spatio-Temporal Behavior of NO$_x$ Storage and Reduction Monolith Catalysts

Robert Clayton, Ashok Kumar, Jin Xu, Michael P. Harold, Vemuri Balakotaiah

Department of Chemical and Biomolecular Engineering, University of Houston

Lean-burn gasoline and diesel-powered vehicles require significant reductions in emissions of nitrogen oxides (NO$_x$) and particulate soot. NO$_x$ Storage and Reduction (NSR) involves the sequential periodic reactive trapping of NO$_x$ and rapid reduction on multi-functional catalysts containing precious metal and storage components. While NSR is effective in achieving high NO$_x$ conversion, elucidation of the selectivity of NO$_x$ reduction to desired product N$_2$ and byproducts such as NH$_3$ and N$_2$O is paramount in optimizing the lean NO$_x$ trap (LNT) or hybrid LNT/SCR systems. A combination of Temporal Analysis of Products (TAP), and bench-scale reactor experiments, and microkinetic modeling is being carried out to elucidate the spatio-temporal features of NSR on monolithic Pt/Ba catalysts.

The regeneration of a model Pt/BaO/Al$_2$O$_3$ monolith catalyst was studied with hydrogen as the reductant to elucidate the reaction pathways. Our results reveal that H$_2$ is very effective in achieving a high time-averaged NO$_x$ conversion on Pt/Ba catalysts but the product distribution (N$_2$, NH$_3$, N$_2$O) is a sensitive function of the operating conditions. Storage and reduction cycles are identified that maximize the NOx conversion and minimize reductant requirements. Experiments with series of monoliths of a range of lengths enabled the construction of spatio-temporal profiles of reactant and product concentrations. The results show that there are two primary competing routes to the desired N$_2$ product; a direct route from the reduction of stored NO$_x$ by H$_2$ (H$_2$ + NO$_x$ $\rightarrow$ N$_2$) or by a sequential route through NH$_3$ (H$_2$ + NO$_x$ $\rightarrow$ NH$_3$; NH$_3$ + NO$_x$ $\rightarrow$ N$_2$). The results revealed H$_2$ is the superior reductant, especially for temperatures below 230 ^{o}C. At higher temperatures the reduction is feed-limited and the difference between the reductants H$_2$ and NH$_3$ is small. The findings are pieced together to establish a phenomenological picture of the spatio-temporal features of the LNT and microkinetic-based description of the regeneration chemistry.

The Seven Steps to Specifying a Hydrogenation Catalyst Bed

Gary Gildert

Custom Catalytic Solution, La Porte, TX

Abstract:

Catalysts are essential in oil refining and in the production of petrochemicals. In a typical refinery, each crude oil fraction passes though two to six different catalyst beds in the transformation to gasoline, diesel, or petrochemical feedstock. At least one of these catalyst beds contains hydrogenation catalyst. Additional catalyst is required to convert hydrocarbon feedstocks to refined petrochemicals.   Specifying the right catalyst bed can mean the difference between years of profitable, trouble-free operation and continuously dealing with "issues" and "opportunities for improvement".
This talk outlines the seven basic steps in specifying a hydrogenation catalyst bed: performance specification, process configuration, catalyst selection, mass balance, heat balance, catalyst volume, and reactor diameter.

Bio:

Gary R. Gildert has worked in the hydrocarbon processing industry for 25 years in plant operations, capital projects, R&D, sales, and technical support. He is an internationally recognized expert in hydro treating with an impressive record of patents, publications, and international presentations.   Mr. Gildert is co-founder of Custom Catalytic Solutions, a new catalyst company located in Pasadena Texas.

Custom Catalytic Solutions, Inc. (www.customcatalytic.com) manufactures high-quality, custom catalysts for the chemical process industry while maintaining an environmentally friendly facility and operating process. The new manufacturing plant is strategically located in Pasadena, Texas, providing ready access to Gulf Coast refineries and petrochemical producers. Their business model ensures that the chemical processing industry will have access to varying quantities of catalyst, quickly, at competitive prices.

Understanding the Interplay Between Dynamics and Reactivity of Organic Layers Deposited on MCM-41

Daniel F. Shantz

Artie McFerrin Department of Chemical Engineering, Texas A&M University

The area of organocatalysis is one that has grown dramatically in recent years. Organic layers attached to model substrates, as heterogeneous catalysts, offer potential opportunities for a deeper mechanistic understanding of organocatalysis. This talk will present an overview of our recent work in using solid-state NMR to probe dynamics and local structure in these systems and rationalize reactivity in the context of the NMR data. I will present results of ^{2}H NMR measurements that study the rotational dynamics of several groups attached to MCM-41, including trimethylsilyl groups, deuterated substituent groups of secondary amines (e.g. labeled benzylamine, methylamine, and piperazine). I will then present results from catalytic testing, including the Aldol and Henry reaction. The overarching goal is to understand the relationship between dynamics and activity and the current work clearly underscores the interplay between them.

Dimensions in Catalyst Design: FCC Feed Hydrotreating Catalysis

L. Burns, G. Anderson, S. Eijsbouts, S. Mayo, K. Riley

Albemarle Corporation, Pasadena, TX

Successful hydrotreating of Fluid Catalytic Cracker (FCC) feedstock is a cost effective and common practice in the refining industry that improves FCC product quality and operation. However, FCC feed pretreating is a complex process that can have varied objectives such as achieving constant product sulfur targets, high aromatic saturation for optimum FCC performance, or moderate boiling point conversion. The feed to the FCC pretreater often has a high boiling point, contaminated with various metals & heavy aromatics and high concentrations of heteroatoms (S, N). Hydrotreating catalysts must be carefully designed and correctly applied to be successful both in terms of meeting product quality targets and providing reliable activity. The catalysts must also allow reliable operations by guarding against potential problems, such as pressure drop problems and flow maldistribution. This paper addresses the design considerations at each scale of the process, from the molecular (crystallite) scale to the reactor scale.

Copper Complexes for Carbon-Silicon Bond Activation: Access to Organocopper Reagents from Stable Organosilane Precursors

Zachary T. Ball

Department of Chemistry, Rice University, Houston, TX

Abstract:

Reactive organometallics are part and parcel of synthetic chemistry. However, traditional organometallics are often unstable, react with air and water, or are intolerant of the presence of functional groups. Organosilanes potentially represent a cheap, robust, and environmentally benign precursor to reactive organometallics, but the nature of the very stable C–Si bond has generally prevented their use as precursors to more reactive organometallics. We have developed a copper complex which activates organosilanes in anhydrous media under mild conditions, effecting transmetallation to produce stable and isolable organocopper species in a functional-group tolerant process. This discovery allows us to better understand the fundamental reactivity of presumed intermediates in copper-catalyzed reactions and to develop new catalytic bond-forming processes of organosilane reagents.

Development of Ce-Zr Nano-oxide Catalysts for Diesel Particulate Filters

K. S. Martirosyan and D. Luss

Department of Chemical and Biomolecular Engineering,

University of Houston, Texas, 77204

The emission of diesel Particulate Matter (PM) poses a serious threat to the human health, particularly in urban areas. The reduction of the PM is accomplished by use of ceramic Diesel Particulate Filter (DPF). The removal of the accumulated PM is still the most challenging aspect of this technology. Due to the relatively low temperatures of the diesel exhaust gas, the current state-of-the-art is to use catalytic assistance to reduce the soot ignition temperature and accelerate its oxidation. The commercial DPFs use Pt as the catalyst that requires an ignition temperature of about 400 °C, requiring post injection of diesel to initiate the oxidation of the PM. Use of precious metal catalysts is an expensive solution. A more economic solution is the use of nano-crystalline complex oxides as the catalyst.

The goals of this research are to develop novel *cost-effective catalytic DPFs* with a lower ignition temperature than the current ones and to increase the DPF life and reliability by the decreasing the PM ignition temperature in catalytic trap. Our synthesis and screening of many nanostructured complex oxides indicates that $Ce_{1-x}Zr_xO_2$ where x=0.1-0.7 and Ag-doped $Ce_{0.5}Zr_{0.5}O_2$ are the most promising candidates to have superior catalytic activity for regeneration of DPFs. The ignition temperatures of these oxides are below 400 ºC so that their activity is comparable with that of commercial Pt-catalysts. We used solution combustion synthesis for one step - *in situ* synthesis and deposition/impregnation of catalyst into the wall-flow diesel particulate cordierite ($2MgO_2{\cdot}Al_2O_3{\cdot}5SiO_2$) filter. This process involves a self-sustained reaction in aqua solutions of metal nitrates and different fuels (glycine, hydrazine, citric acid) which can be classified based on their chemical structure, i.e. type of reactive groups (amino, hydroxyl, carboxyl) bonded to the carbon chain. These fuels provide high temperature rapid interaction in the system, reacting with oxygen containing species formed during the metal nitrates decomposition. This method is shown to be an efficient and cost-effective method for catalyst deposition.

Global Kinetics for NO Reduction and CO & H_2 Oxidation in Monolith Reactors

Divesh Bhatia[1], Michael P. Harold[1] and Vemuri Balakotaiah[1]

[1] *Department of Chemical and Biomolecular Engineering, University of Houston, 4800 Calhoun Road, S222 Engineering Bldg 1, Houston TX, 77204 USA*

1. Introduction

In spite of many years of research on catalytic converters, the scientific community does not agree on a single reaction mechanism involving NO, CO and H_2 on a supported catalyst such as Pt/Al_2O_3. Most of the modeling studies reported in the literature utilize either a global kinetic rate expression originally proposed by Oh and Cavendish [1], or some variations of it. The reaction kinetics originally proposed for a stoichiometrically lean system may not be valid for a rich system. In addition, the pre-exponential factors and activation energies of CO and H_2 oxidation are assumed to be the same. Our modeling studies have shown that such an assumption predicts simultaneous light-off of CO and H_2 which is contrary to the results observed experimentally [2]. H_2 oxidation on a Pt catalyst is found to occur at room temperature, but the rate expression for H_2 oxidation [1] does not predict the same. The kinetics for NO reduction by H_2 [3] predict a positive order rate with respect to NO, whereas experimental results [4] show a delay in light-off with addition of NO.

2. Present work

In this study, we use a "short monolith" reactor model, which has been shown to capture the main qualitative trends of an integral reactor [5], besides having the advantage of a lower computation cost than the two-phase integral reactor models. It is obtained by integrating the conventional integral reactor equations, and applying the appropriate boundary conditions. The non-isothermal behavior of the system has been taken into account in the current model and heat loss to the surroundings has been neglected. We use a detailed microkinetic mechanism, originally proposed by Chatterjee et al. [6] and modify it to predict the key trends of the CO-H_2 oxidation system, the main being prediction of H_2 ignition at room temperature, inhibiting effect of CO on H_2 light-off and the enhancement effect of H_2 on CO light-off. Also, a small amount of H_2 reduces the ignition temperature significantly, whereas the benefit of

adding more H_2 is small. We have proposed that the activation energy of CO desorption decreases with an increase in the coverage of H species on Pt, thus explaining the creation of more sites for oxygen adsorption. Based on the microkinetic studies and experimental results available in the literature, modifications have been made to the global kinetics, which currently do not contain the effect of H_2 on CO oxidation kinetics. Global reaction kinetics have also been proposed for the reduction of NO by H_2 on a Pt/BaO/Al$_2$O$_3$ catalyst, under anaerobic and aerobic conditions. The model predicts a delay in light-off with addition of NO, which is not predicted by the model proposed by Tsinoglou and Koltsakis [3]. Also, a maximum in NO conversion with temperature is predicted for lean conditions.

References:
1. S.H. Oh & J.C. Cavendish, *Ind. Eng. Chem. Prod. Res. Dev.*, **21**, 29-37 (1982).
2. S. Salomons, M. Votsmeier, R.E. Hayes, A. Drochner, H. Vogel, & J. Gieshof, *Catalysis Today*, **117**, 491-497 (2006).
3. D. Tsinoglou & G.C. Koltsakis, *Chem. Eng Sci.*, **58**, 179-192 (2003).
4. R.D. Clayton, M.P. Harold, & V. Balakotaiah, *Applied Catalysis B: Environmental*, **81**, 161-181 (2008).
5. V. Balakotaiah, N. Gupta, & D.H. West, *Chem. Eng. Sci.*, **55**, 5367-5383 (2000).
6. D. Chatterjee, O. Deutschmann, & J. Warnatz, *Faraday Discuss.*, **119**, 371-384 (2001).

In Situ Investigations of CO Oxidation on Pt-Group Metal Catalysts: From Ultrahigh Vacuum to Elevated Pressures

Yun Cai, Feng Gao, Kerrie Gath, D. Wayne Goodman

Department of Chemistry, Texas A&M University

CO oxidation reaction on Pt-group metals was studied both at low CO pressures under steady-state conditions ($\leq 1\times10^{-5}$ Torr) and high pressures (0.01-10 Torr) at various CO/O_2 ratios. Surface CO species were probed with in situ polarization modulation infrared reflection absorption spectroscopy (PM-IRAS), and CO and O coverages were estimated using the combination of PM-IRAS and X-ray photoelectron spectroscopy. CO titration experiments were also carried out on surfaces with known oxygen coverages. These experimental results were used to make correlations between reaction kinetics and surface reactant species. The most active phase has been found to be chemisorbed oxygen. A surface oxide phase is also active in CO oxidation while a bulk oxide is inert.

NO_x Storage and Reduction with H_2 on Pt/BaO/Al$_2$O$_3$ Monolith: Spatio-Temporal Resolution of Product Distribution

R. D. Clayton, V. Balakotaiah and M. P. Harold

Department of Chemical and Biomolecular Engineering
University of Houston, Houston, TX 77204-4004

Lean burn engines are more fuel efficient than stoichiometrically operated gasoline engines. However, the unconverted oxygen in diesel vehicle exhaust prevents the use of conventional three-way catalysts to reduce NO_X to N_2. During the past decade there has been an increased interest in the development of exhaust after-treatment systems for lean NOx reduction. NO_X Storage and Reduction (NSR) has been shown to be an effective technology. NSR is a periodic catalytic process for converting NO and NO_2 (NO_x) to N_2 in the exhaust of lean burn and diesel engines. The NO_X removal process involves two stages on a bifunctional supported catalyst. The first stage involves storage of NOx on an alkali earth component (such as Ba, K) mediated by a precious metal (Pt, Rh). The second stage involves purging by a shorter exposure of rich pulse when an unacceptable amount of NO_x is released. The close coupling between the Pt and Ba is very important in both the storage and regeneration stages. The rich pulse is created through intermittent rich operation of the engine, producing a mixture of H_2, CO, and low molecular weight hydrocarbons.

The regeneration of a model Pt/BaO/Al$_2$O$_3$ monolith catalyst was studied with hydrogen as the reductant to elucidate the reaction pathways to molecular nitrogen, either by direct NOx reduction with hydrogen or indirect reduction through intermediate ammonia. NOx storage and reduction experiments (NSR) were conducted with a 2 cm length monolith for a wide range of feed conditions. The NSR experiments were replicated for a series of monoliths of progressively decreasing length (2.0, 1.33, 1.0, 0.67 and 0.33 cm), enabling the construction of spatio-temporal profiles of reactant and product concentrations. The results show that there are two primary competing routes to the desired N_2 product; specifically a direct route from the reduction of stored NOx by H_2 (H_2 + NOx $\rightarrow$ N_2) or by a sequential route through NH_3 (H_2 + NOx $\rightarrow$ NH_3; NH_3 + NOx $\rightarrow$ N_2). A comparison between H_2 and NH_3 as reductant feeds during NSR revealed H_2 is a more effective reductant in terms of NOx conversion for temperatures

below approximately 230 $^{\circ}$C. At higher temperatures (230 to 380 $^{\circ}$C), the reduction is feed-limited and the difference between the reductants H_2 and NH_3 is found to be small with H_2 being a slightly superior reductant.

Experimental measurements of the traveling front velocity are compared with a simple feed-limited model that assumes complete consumption of H_2 as stored NOx is depleted. The reactor data helped to elucidate the time- and space-dependent concentration profiles as well as an overall reaction network during lean NOx trap operation with hydrogen as the reductant.

Finally, the effect of Pt dispersion (3, 10, 50%) was studied for a fixed Pt loading to help elucidate the role of the Pt-Ba coupling. During storage the difference in the catalysts was greatest at lower temperatures (< 200 $^{\circ}$C) due to the kinetic limitations of NO oxidation. The higher dispersion catalyst is more effective in storing NOx at low temperatures, presumably due to the higher Pt/BaO interfacial perimeter, which allows for more NOx to spillover. At higher temperatures the difference in NOx storage is smaller between the different catalysts. Similarly, during regeneration the NOx conversion rate is more sensitive to the Pt dispersion at lower temperatures. These data provide useful information about the systematic study helps in understanding the close coupling of Pt and BaO in NOx storage and reduction catalyst.

Ketonization - Catalyst Comparisons With and Without Water in Feeds

Freddy Avila Diaz , Kerry Dooley

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This project is a continuation of our previous work in developing robust condensation catalysts for condensations of acids, aldehydes and alcohols. We have discovered that in condensations to make methylketones, increased partial pressures of water can sometimes improve catalyst selectivity for decarboxylative condensation. We are examining this effect for two interesting catalyst classes, CeO_2/Al_2O_3 and K_2O/TiO_2. Results for acetic acid decarboxylative condensation and acetone aldol condensation are presented and explained in terms of spectroscopic characterization (XPS and in-situ XAFS and XANES).

Immobilization and Testing of Pd-on-Au Nanoparticles for Catalyzed Trichloroethene Hydrodechlorination in Water

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Trichloroethene (TCE) is one of the most common hazardous organic contaminants found in groundwater. Its use as a solvent in the automotive, metals, electronic and other industries has led to prevalence in our environment. TCE has been linked to liver damage, impaired pregnancies, and cancers in humans. Compared to conventional physical displacement methods of air-stripping and carbon adsorption, remediation through the catalytic breakdown of TCE molecules is a more effective and desirable approach. In our previous work, palladium-on-gold nanoparticles (Pd/Au NPs, 4 nm or 20 nm) has been shown to catalyze the TCE hydrodechlorination (TCE HDC) in water, at room temperature, and in the presence of hydrogen, with the most active Pd/Au NPs (k = 1900 $L/g_{Pd}/min$) found to be >70 times more active than conventional Pd-on-alumina (1% Pd/Al_2O_3) (k = 26 $L/g_{Pd}/min$) on a per-Pd atom basis.

Here, we improve the potential of this Pd/Au NP catalyst for groundwater remediation by immobilizing the NPs on a solid support. Immobilization is an important issue of sustainable nanomaterials in water treatment. Once the active NPs can be immobilized on a solid support, long-term continuous systems become feasible. To achieve NP immobilization, we used ion exchange resin (IER) beads as the solid support. IER is an insoluble crosslinked polystyrene matrix with surface sites which can easily trap and release ions in a process called ion-exchange.

We present two strategies for immobilization: (1) direct NP immobilization, and (2) direct synthesis of NPs onto IER's. Preliminary results indicate one type of Pd/Au/IER particles can have activities as high as 1017.6 $L/g_{Pd}/min$.

Reactivity of CO on Oxygen-Saturated Rh and Pd Surfacee: An X-Ray Photoelectron Spectroscopic Study

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CO oxidation is of fundamental and practical importance to many industries such as automotive, energy production, and fuel cell development. The reduction of Rh and Pd saturated with chemisorbed oxygen by CO was studied using X-ray photoelectron spectroscopy (XPS). The reaction probability for CO oxidation was then calculated by deconvoluting the oxygen and metal peaks into their separate components. Previously, using polarization modulation reflectance absorption infrared spectroscopy (PM-IRAS) and XPS, CO oxidation was found to be more reactive on Pt-group metals with a saturated layer of chemisorbed oxygen. This chemisorbed oxygen surface is highly active, where a turnover frequency for CO oxidation of some 2-3 orders of magnitude higher than that for the corresponding metal surface is achieved by running the reaction in excess O_2 (O_2/CO ratio >0.5).

In-situ Monitoring of Catalyzed Aqueous-Phase Trichloroethylene Hydrodechlorination using Pd-on-Au Nanoshells via Surface-Enhanced Raman Spectroscopy

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In situ characterization of the adsorption and reaction of chemicals in aqueous systems over heterogeneous catalysts has been a long been a challenge. While methods such as electron energy loss spectroscopy have been used successfully to monitor to the adsorption of compounds to model catalyst sites, they rely on ultra high vacuum environments. While FTIR coupled with ATR techniques can offer more realistic conditions, the penetration depth of such spectroscopy is on the bulk level, and signals produced suffer from the strong absorption of the aqueous environment. Surface-enhanced Raman spectroscopy (SERS) using gold nanoshells, on the other hand, could provide the requisite sensitivity for analyzing aqueous-phase catalyzed reactions. Au nanoshells are a class of SERS substrates, whose surface plasmon resonance (SPR) can easily be tuned by modifying core particle size and shell thickness, resulting in signals up to 10^{14} times greater than normal Raman alone.

The aqueous-phase hydrodechlorination (HDC) of trichloroethylene (TCE) has been shown to be highly efficient using newly developed Pd-on-Au nanoparticles (Pd/Au NPs), leading to ethane and chloride ions. These materials also are highly effective for other chlorinated ethylenes. In this paper, we report the synthesis of Pd-decorated Au nanoshells to mimic the HDC catalytic behavior of Pd/Au NPs during SERS analysis and the development of the SERS cell chamber. Preliminary SERS spectral analysis indicates that chemisorption and HDC surface reaction events of dichloroethylene (DCE) probe molecule can be observed. It appears that 1,1-DCE adsorbs to the Pd catalyst via pi-bonding with Pd atoms on the surface, for example. The results of this study highlights the promising use of SERS spectroscopy of metal-catalyzed reactions in water in situ.

Generation of High Purity Hydrogen from Ammonia Decomposition using Nanopore Palladium Membrane Based Catalytic Reactors

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"Pd nanopore" composite membranes are a novel class of H_2 permselective membranes in which a thin layer of Pd is grown within the pores of a supported nanoporous layer. In this work, Pd nanopore membranes and conventional Pd top-layer membranes were used in the generation of high purity H_2 from the catalytic decomposition of anhydrous NH_3. A 4 μm Pd nanopore membrane and a 13 μm Pd top-layer membrane were synthesized on 2 mm o.d. α-Al_2O_3 hollow fibers. The permeation features of the membranes were determined and used in a single fiber packed bed membrane reactor using Ni-catalyzed NH_3 decomposition as the test reaction, with conditions spanning 500 - 600 ^{o}C, 3-5 bar total retentate pressures and 60-1200 scc/hr gm cat space velocity. The NH_3 conversions in both the PBMRs were approximately 10 % higher than in a packed bed reactor (PBR) under similar conditions. The increase in conversion with the PBMR was attributed to the removal of H_2, which has an inhibitory effect on the forward kinetics of the reaction as per the Temkin-Pyzhev type rate mechanism. Reactor productivities in the range of 2 mol/s m^3 (at 85% H_2 utilization) to 7 mol/s m^3 (at 50 % H_2 utilization) were obtained. The permeate stream purity exceeded 99.20 H_2. A two-dimensional pseudo-homogeneous model was successfully used to simulate the experimental results and to interpret the findings. The 2-D model predictions and an analysis of the characteristic times of the various processes involved were used to determine the rate limiting step and to suggest ways in which the reactor productivities could be further improved.

Low-Dimensional Models for Real Time Simulations of Catalytic Monoliths

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The monolith catalytic reactor is widely used in auto exhaust treatment and other applications. It has several advantages (such as high heat and mass transport rates per unit pressure drop, smaller transverse temperature gradients and ease of scale-up) compared to the traditional packed-bed reactor. The monolith reactor consists of a large number of long, narrow channels in parallel through which reacting fluid flows and catalyst is deposited in the form of washcoat on the wall of the monolith. The reactants diffuse transverse to the flow direction in the gas phase and through porous washcoat where they react and products formed diffuse back into the gas phase. There exists a complex nonlinear interaction between chemistry and transport processes occurring at different length (or time) scales. This strong coupling at smaller scales influences the reactor behavior and process performance at macro scale. Therefore, it is essential to solve detailed model equations from reactor (macro) scale down to local diffusional (micro) scale in order to capture micro scale effects. The solution of the detailed model equations from macro scale down to micro scale is numerically intensive. Moreover, it has limited use in reactor control, optimization and studying bifurcation features.

In this work, we present new simplified low-dimensional models for real time simulation, control and optimization of catalytic converters used in automobiles. Liapunov-Schmidt (LS) technique of bifurcation theory is used to obtain the simplified models. Specifically, we reduce the transverse degrees of freedom by averaging the convection-diffusion-reaction equations in the transverse direction to obtain multi-mode models that are generalizations of the classical two-phase models. The resulting low-dimensional models are described by a system of differential algebraic equations involving multiple concentration and temperature modes. These "multi-mode models" capture all the important features involving exchange of mass and thermal energy between different phases. We use this model for simulation of three way converter (TWC) and compare the solution obtained with detailed model solution. It is observed

that there is a very good agreement between both the predictions. Since the solution of low dimensional models requires considerably less computation time while retaining all the parameters and essential physics of the detailed model, they can be used for accurate design and control of catalytic monoliths used in automobiles.

Removal of H_2S Using Regenerable Sorbents of Rare Earth/Transition Metal Oxides

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Current materials for high temperature H_2S removal from gasifier effluents are Zn- and Ca-based sorbents. These work at temperatures less than typical effluent temperatures. We are examining sorbents based on Ce/La/M (M = transition metal) oxides and Ce/La/RE (RE = a rare earth) oxide. Reduced Ce/La oxides adsorb H_2S at temperatures of 600°C and above, and are regenerable in O_2 mixtures. But addition of group VII-VIII transition metals to Ce/LaOx increases the sulfur removal capacity significantly. Addition of oxides such as ZrO_2 or a third rare earth oxide increases surface area, sintering resistance of CeO_x/La_2O_3 at high temperatures, and sulfur capacity. These sorbents can be regenerated at temperatures near the operating conditions of gasifiers. They can also be used as tar cracking catalysts for tars formed in the gasifier. The results of several characterization tests, including H_2S adsorption / TPD, are presented.

TAP Studies of NO$_X$ Storage and Reduction on Variable Dispersion Pt/BaO/Al$_2$O$_3$ Catalysts

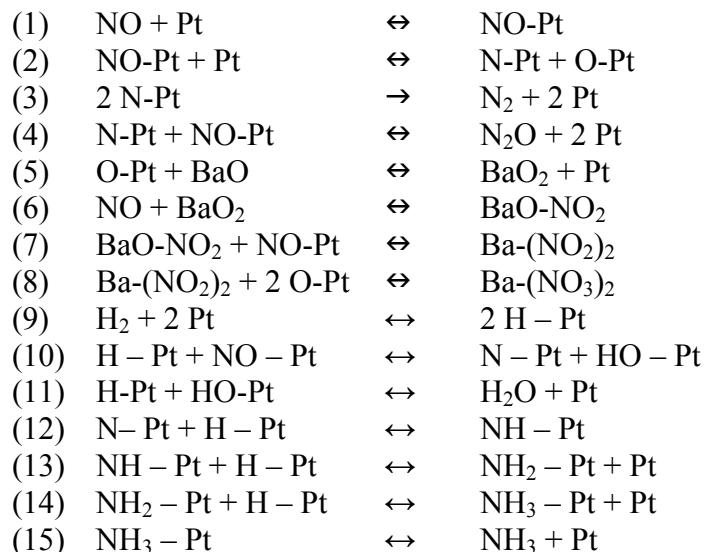Ashok Kumar, V. Balakotaiah, Michael P. Harold

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NO$_X$ emission from diesel vehicles is a significant environmental problems affecting major urban areas. NO$_X$ Storage and Reduction (NSR) is an emerging technology that overcomes the difficulty of accomplishing NO$_X$ reduction in a lean exhaust. The NO$_X$ removal process involves two stages on a bifunctional catalyst in the lean NO$_X$ trap (LNT). The first stage involves storage of NO$_X$ on an alkali earth component (Ba, Ca) mediated by precious metal (Pt, Rh). The second stage involves the injection of a rich pulse of shorter exposure to reduce the stored NO$_X$. In this study we employ Temporal Analysis of Products (TAP) experiments and microkinetic mechanistic modeling to further the understanding of NSR. TAP experiments are carried out isothermally in the Knudsen transport regime thereby avoiding complicating thermal and mass limitations encountered in atmospheric pressure studies.

The TAP studies involve feeding reactant pulses to model Pt/BaO/Al$_2$O$_3$ (3 - 30 % Pt dispersion, 2-3 wt.% Pt, 15 wt.% BaO) and Pt/Al$_2$O$_3$ (1.5 wt% Pt with 30 % dispersion) catalysts at ~10^{-8} torr pressure over the 150 $^{\circ}$C - 400 $^{\circ}$C temperature range. Two kinds of experiments are performed; storage-pulsing experiment, in which NO is pulsed with spacing time (τ_s), and pump-probe experiment in which NO and H$_2$ are sequentially pulsed with a prescribed delay time (τ_d) and spacing time (τ_s). The product gas emerging from the catalyst bed is analyzed by a Quadrupole Mass Spectrometer (QMS) in a separate chamber maintained at ~10^{-8} torr. The QMS monitors effluents N$_2$, NO, NH$_3$, N$_2$O, H$_2$ and H$_2$O. The feed intensities are selected to ensure Knudsen transport. Post-reaction TPD is performed to quantify the adsorbed species coverages.

During NO pulsing experiments on Pt/Al$_2$O$_3$, NO decomposes forming N$_2$ as the dominant product with O adatoms accumulating on the Pt (reactions 1-3 below), which leads to a decrease in the decomposition rate and corresponding breakthrough of NO.

Secondary product N_2O achieves a maximum at the NO breakthrough (reaction 4). At lower temperatures adsorbed NO strongly inhibits the reaction. The NO decomposition rate increases with temperature with negligible reaction at 150 $^{\circ}$C. In the presence of BaO, NO_X is stored as nitrite or nitrate by synergistic transfer of NO and O from Pt to Ba (reactions 5-8). The NO_X storage increases as temperature increase with almost no storage at 150 $^{\circ}$C.

(1)	$NO + Pt$	$\leftrightarrow$	$NO\text{-}Pt$
(2)	$NO\text{-}Pt + Pt$	$\leftrightarrow$	$N\text{-}Pt + O\text{-}Pt$
(3)	$2\ N\text{-}Pt$	$\rightarrow$	$N_2 + 2\ Pt$
(4)	$N\text{-}Pt + NO\text{-}Pt$	$\leftrightarrow$	$N_2O + 2\ Pt$
(5)	$O\text{-}Pt + BaO$	$\leftrightarrow$	$BaO_2 + Pt$
(6)	$NO + BaO_2$	$\leftrightarrow$	$BaO\text{-}NO_2$
(7)	$BaO\text{-}NO_2 + NO\text{-}Pt$	$\leftrightarrow$	$Ba\text{-}(NO_2)_2$
(8)	$Ba\text{-}(NO_2)_2 + 2\ O\text{-}Pt$	$\leftrightarrow$	$Ba\text{-}(NO_3)_2$
(9)	$H_2 + 2\ Pt$	$\leftrightarrow$	$2\ H-Pt$
(10)	$H-Pt + NO-Pt$	$\leftrightarrow$	$N-Pt + HO-Pt$
(11)	$H\text{-}Pt + HO\text{-}Pt$	$\leftrightarrow$	$H_2O + Pt$
(12)	$N-Pt + H-Pt$	$\leftrightarrow$	$NH-Pt$
(13)	$NH-Pt + H-Pt$	$\leftrightarrow$	$NH_2-Pt + Pt$
(14)	$NH_2-Pt + H-Pt$	$\leftrightarrow$	$NH_3-Pt + Pt$
(15)	NH_3-Pt	$\leftrightarrow$	$NH_3 + Pt$

NO/H_2 pump probe experiments on Pt/Al_2O_3 with excess H_2 indicate the reaction between adsorbed NO and H_2 at 150 $^{\circ}$C, forming primarily NH_3 (reactions 9-15). At this temperature, negligible N_2O is formed, confirming that the slow NO bond scission (reaction 2) limits N formation required for N_2O. In the presence of BaO, it forms N_2 and NH_3 in 1:3 ratios without any storage of NO on BaO. At higher temperature, N adatoms combination leads to produce N_2 resulting in a decrease in NH_3 production. The storage of NO_X on BaO increases with temperature.

Ongoing experimental results will be presented that compare the performance of Pt and Pt/Ba catalysts having different Pt loadings and dispersions. In particular, we report results for a series of Pt/Ba catalysts with fixed Pt loading and varied dispersion.

Stabilized and Enhanced PtCu₃/C Oxygen Reduction Electrocatalysts via Au Galvanic Displacement

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ABSTRACT

Dealloyed PtCu₃/C catalysts have shown 3-4 times higher mass and specific activities for oxygen reduction over pure Pt/C catalysts [1]. Most recently, Zhang et al. [2] reported that Au clusters had a stabilizing effect on an underlying Pt metal surface and suppressed Pt dissolution during the potential cycling. The Au clusters were deposited on Pt/C catalysts through galvanic displacement of a Cu monolayer on Pt obtained under-potential deposition (UPD)[3]. We reported here that the enhanced electrocatalytic oxygen reduction activity of PtCu₃/C catalysts was stabilized using Au galvanic displacement of Cu in PtCu₃/C. The results showed that mass activities decreased by 24 and 29%, and specific activities decreased by 6 and 26% for Pt/C and PtCu₃/C catalysts, respectively, while PtCu₃/C modified by Au can retain both mass and specific activities after 1000 potential cycles between 0.6 and 1.0V vs RHE. XRD patterns showed that additional peaks related to Au-riched phase appeared, while the peaks related to PtCu alloy phase didn't change much. In combination with XPS analysis, Cu in PtCu₃/C catalysts was displaced spontaneously by Au^{3+}. EDS analysis combined with HRTEM showed big particles were enriched with Au, while small particles were enriched with Pt. STEM showed Pt-Au shell Pt-Cu core structures. Au atoms in PtCu₃/C catalysts affected electronic structure of Pt-enriched shell, and therefore improved the ORR activity compared to the dealloyed PtCu₃/C catalysts. On the other hand, Au atoms inhibited Pt oxidation and helped to keep favorable Pt-Pt distances created by dealloying, thus improving the stability of ORR activity on PtCu₃/C catalysts.

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Mechanochemical Synthesis of Novel Nanoparticle Catalyst

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Abstract

A heterogeneous catalyst's performance is critically dependent on the process of its creation. Heterogeneous catalysts are generally created sequentially (ex. synthesis, stabilization, and activation) which require elevated temperatures. Mechanochemistry and mechanochemical processing offer the relatively unexploited potential for the creation of unique catalysts at nearly ambient temperatures for in situ synthesis, stabilization and activation while allowing for the possibility of additional requisite thermal treatments. This approach can offer unrestricted compositions, large surface areas, high surface energies, incorporation of heterogeneous catalyst's components and nanostructures that are difficult to achieve by other technologies. Mechanochemistry offers rudimentary approaches to yield metal matrix composites, oxide matrix metal composites, nonmetal catalysts such as refractory compounds (borides, carbides, nitrides, silicides, etc.), intermetallics, bi- and multicomponent alloys, amorphous materials, immobilized homogeneous and enzyme catalysts, and functional composites for a multitude of specific reactions. The relative simplicity of the syntheses of nanostructure model catalytic systems allows both the rapid production and study with systems of modern materials and surface characterization tools. The principles of mechanochemical engineering are outlined with results from recent studies of nanostructured non-metallic and immobilized homogeneous catalyst systems. The effect of milling time, composition, milling aids and sequence of steps on the formation of amorphous to crystalline phases has been studied using X-ray diffraction (for phase identification and speciation) and thermal analysis.   Further characterizations have been carried out by particle size distribution and analytical scanning electron microscopy (SEM) with energy dispersive analysis of X-rays (EDAX). The results will be discussed on how high energy ball milling of main group metallic and transition metals gives us the ability to produce novel nanosized intermetallic catalysts.

Pt-M and Pt-M$_1$-M$_2$ core-shell electrocatalysts for oxygen reduction reaction in PEMFC

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Dangers of post oil peak scenario, political uncertainty, greenhouse emissions and consistently increasing oil prices have impacted several growing economies. Thereby there is need to move to alternative cleaner and abundant sources of energy. One of the alternatives is a hydrogen economy. Hydrogen fuelled proton exchange membrane (PEMFC) fuel cells have consistently demonstrated great promise as future source of energy due to their high conversion efficiency, lower temperature of operation and lack of greenhouse emissions. Till now Pt has been found to be the best electrocatalyst for the oxygen reduction reaction (ORR) due to higher electrocatalytic activity and stability. One of the major impediments in the commercialization of polymer electrolyte membrane fuel cell is the low activity and higher loading of Pt electrocatalyst used for oxygen reduction. The quest for more active, less expensive and highly stable ORR catalyst thrives the fuel cell research from Pt dispersed contemporary catalyst to Pt alloys. In recent years lot of emphasis has been put on Pt alloy catalysts because of even higher activity and lower cost as compared to Pt catalysts only.

In this work we demonstrate Pt-alloy catalysts as nanoparticles supported on carbon as ORR catalysts in PEMFC. These catalysts are prepared to liquid based impregnation and thermal annealing route. We have done half cell measurements on these catalysts in a RDE and full characterization in single cell PEMFC. To obtain the active phase of our catalyst we do in-situ as well as ex-situ pretreatment. The in-situ method is the electrochemical de-alloying while the ex-situ is the chemical de-alloying. Our Pt$_{25}$Cu$_{75}$ have consistently shown enhanced activity [1,3,4], Pt$_{20}$Cu$_{20}$Co$_{60}$ [2] has also shown promising results. We have further done durability analysis on these catalysts in real PEMFC's by potential cycling under different humidity and potential window conditions. EPMA analysis of the cross-section of as prepared MEA's, de-alloyed MEA's and tested MEA's shown the migration of Pt and Cu over the crossection of the MEA.

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2. Prasanna Mani, **Ratndeep Srivastava** and Peter Strasser, "De-alloyed PtCu core shell nanoparticle for use in PEM fuel cell cathodes," In press 10.1021/jp0776412, Journal of Physical Chemistry C.

3. Prasanna Mani, **Ratndeep Srivastava**, Chengfei Yu, and Peter Strasser "*In situ* inlayer dealloying of Pt-M intermetallics for high performance PEMFC electrode layers: MEA activity and durability studies" Polymer Electrolyte Membrane Fuel Cells 7, *Electrochemical Society Transactions* (2007).

4. Shirlaine Koh, Chengfei Yu, Prasanna Mani, **Ratndeep Srivastava**, Peter Strasser, "Activity of ordered and disordered Pt-Co alloy phases for the electro reduction of oxygen in catalysts with multiple coexisting phases" , 72 (1), Oct 2007,50-56

Scanning Tunneling Microscopy for Model Catalytic Studies

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We report our recent advances in applying scanning tunneling microscopy (STM) in model catalytic studies with the ability to 1) monitor the surface of working catalysts under realistic conditions, i.e., elevated reactant pressures and temperatures, and 2) obtain the atomic structure of molecular-sized supported catalysts. In this study, we have been able to monitor the surface change of Rh (110) during CO oxidation. Simultaneous measurements of reaction rates and scanning tunneling spectroscopy (STS) could further relate the surface oxidation states with surface reactivity. We have also explored the characterization of supported molecular catalysts. One particular system, namely Ru_3Sn_3, an efficient catalyst for selective hydrogenation, will be highlighted. This mixed-metal cluster has been deposited onto a thin silica film surface using a wet impregnation method similar to that used in the preparation of industrial catalysts. STM has then been employed to reveal the atomic structure and stability of the supported Ru_3Sn_3 clusters.

Modeling of Catalytic NO Reduction by H_2 and NH_3 in O_2 on Pt/Al_2O_3

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Abstract – The NO_x trap monolithic catalytic reactor is emerging as a promising technology for meeting the increasingly stringent restrictions on vehicular emissions from lean burn and diesel engines. The NO_x trap is a multi-functional catalytic (Pt/BaO/Al_2O_3) reactor operated periodically between lean and rich conditions. During the lean operation, the NO_x is stored on an alkali earth oxide as nitrites/nitrates and reduced during the rich operation period, which is usually much shorter than the lean period. Successful design and operation of the NO_x trap requires understanding the fundamental mechanisms and kinetics of storage and reduction and their coupling with the transport processes.

The influence of hydrogen on NO_x trap performance is of interest because H_2, produced by water gas shift reaction, presents an important component in the exhaust and is an efficient reductant for NO, especially, at lower temperatures. The reduction of NO with H_2 over noble metal catalysts produces a complex mixture of N_2, N_2O, and NH_3. Recent studies have shown that NH_3 oxidation by NO and O_2 may be important in the NO_x trap. In this study, a short monolith model has been developed to validate the hypothetical reaction pathway of N/H/O system on Pt. The short monolith model allows us to include both mass transfer and detailed chemistry describing the adsorption, desorption, storage and surface reaction steps for the various species. The calculation results are compared with steady-state experimental findings for NO/H_2, NH_3/NO/H_2 and NH_3/O_2 systems.

Carbon Support Effects on Oxygen Reduction Fuel Cell Electrocatalysts by Voltammetric Surface Dealloying

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State-of-the-art proton exchange membrane (PEM) fuel cells encountered performance and durability challenges associated with two major key materials, e.g. PEMs and electrocatalysts, although anticipated to be approaching their most attractive automobile application. The carbon supported platinum (Pt/C) catalyst was widely employed in fuel cell cathode for oxygen reduction reaction (ORR) for decades. However, the development of high activity and low cost noble metal catalyst would be much favorable for PEM fuel cell applications. Recently, our group investigated carbon supported bimetallic Pt-Cu and trimetallic Pt-Cu-Co nanoparticles by voltammetric surface dealloying for fuel cell ORR electrocatalysis, which demonstrated the ORR catalytic activity at 0.9 V outperformed the pure Pt/C by a factor of 4-6 times (Shirlaine Koh, et al., J. Am. Chem. Soc., **2007**, *129*, 12624. Ratndeep Srivastava, et al., Angewandte Chemie, **2007**, *46*, 8988). Since alternative carbon support materials possess good electrical conductivity, thermal and chemical stability, ability of surface modification, controllable porosity and recovery capacity of supported noble metal catalyst through burning away the carbon support, etc, it was widely used for catalyst support. Especially, for the fuel cell ORR electrocatalyst, the employed carbon support should be of high chemical/electrochemical stability, good electronic conductivity, and high surface area and pore size distribution (Zhufang Liu, et al., Journal of Power Sources, **2007**, *164*, 472.).

Herein, aiming at extended investigation of carbon supported bimetallic Pt-Cu catalyst by voltammetric surface dealloying, we report carbon support effects on this catalyst activity. The electrocatalyst was synthesized by two-step process, including preparation of carbon supported Pt-Cu precursor (Pt/Cu atom ratio of 1:3, $PtCu_3$) followed by

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electrochemical dissolution/dealloying surface Cu component. The carbon supported Pt-Cu precursor was synthesized by immersing commercial Pt/C catalyst into copper nitrate solution, dispersing to form homogenous ink, frozen in liquid nitrogen bath, drying in freeze drier, and annealed at 600 - 800 ^oC under 6% H_2/Argon mixture circumstance. The selected carbon support materials were from Tanaka K.K. (TKK) 28.1 wt% Pt/HSC and 28.7 wt% Pt/Vulcan. The carbon supported Pt-Cu catalyst derivative from various carbon support were compared, based on ORR catalytic activity through thin-film rotating disk electrode (TF-RDE), and structure characterization through X-ray diffraction (XRD) measurements.

Table 1 ORR activity measurements of Pt-Cu/C catalyst by RDE

$PtCu_3$/C catalyst precursor code	Description	ECSA / m^2/g	Mass activity @ 0.9V / A/mg Pt	Specific activity / μA/cm^2 Pt
F 104	TKK 28.7% Pt/Vulcan, 600 ^oC	48.9	0.289	591
F 105	TKK 28.7% Pt/Vulcan, 800 ^oC	26.0	0.254	979
G 0043	TKK 28.1% Pt/HSC, 800 ^oC	52.0	0.417	801

Shown in Table 1 is the mass activity of our dealloyed Pt-Cu/C catalyst based on HSC support was almost 1.5 - 2 times that based on Vulcan support. This is attributed to the higher surface area of HSC than Vulcan, referred by the BET (Brunauer, Emmett and Teller) surface area of TKK 46.6% Pt/Vulcan with 105 m^2/g and TKK 45.95% Pt/HSC with 425 m^2/g (Mei Cai, et al. Journal of Power Sources, **2006**, *160*, 977). The lower surface area maybe contributed to less adsorption of Cu precursor on carbon support during mixing and freeze drying process, which, in turn, lead to lower level alloying of Pt and Cu metal during annealing process.

The XRD measurement was employed to characterize the catalyst structure. Shown in Fig. 1 is X-ray diffraction profiles of PtCu3 precursor catalysts supported by various carbon annealed at various temperature. From the figure, it could be clearly seen that

the shift of the strong Pt-Cu (111) reflections (at $2\theta=42.2^{o}$, 42°) of samples G 0043 and F 105, to higher angles compared to pure Pt (111) peak (at $2\theta=39.7^{o}$), indicates that Pt-Cu alloy with reduced Pt-Pt interatomic distance. With higher temperature, the Pt (111) peaks appears narrower showing larger particles. It should be noted that the Cu peak at (at $2\theta=43.2^{o}$) of sample G 0043 was less distinctive that other two samples F 104 and F 105, which was attributed to the better alloying of Pt-Cu of Pt-Cu/C catalyst based on HSC than those based on Vulcan.

In summary, the effect of carbon support on bimetallic Pt-Cu/C catalyst by electrochemically voltammetric surface dealloying for fuel cell ORR, was preliminarily investigated through TF-RDE, and the catalyst structure confirmed by XRD measurements. The HSC carbon supported Pt-Cu catalyst behaved better catalytic activity, and was of smaller metal particle than Vulcan carbon support. The more selected carbon support materials, and the catalytic activity tested in H2/O2-fed fuel cell would be conducted in the near future.
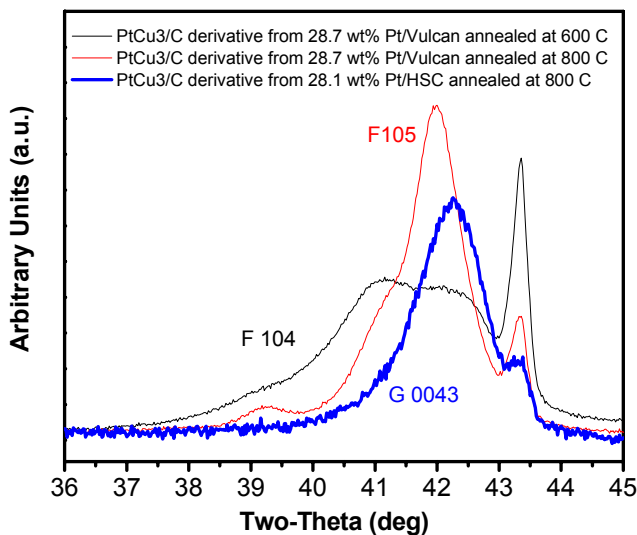

Fig.1   X-ray diffraction profiles of PtCu3 precursor catalysts supported by various carbon annealed at various temperature.