2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Development of Pollution Prevention Technologies

Date: 05/22/13
Technology Area Review: Biodiesel
WBS: 7.7.2.18

Principal Investigator: Roberto Sanchez-Delgado & Jürgen Polle

Organization: Brooklyn College of CUNY

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Goals Statement

1. The development of new nano-structured catalytic materials designed to reduce the amount of pollutants in transportation fuels (fossil and biodiesel) through hydrogenation reactions involving novel heterolytic mechanisms.
2. Assessment of new microalgae strains for potential use as high-quality feedstocks in biofuels applications and analysis of metabolism of algae.

Quad Chart Overview

Timeline

- Project start date: 08/31/2010
- Project end date: 03/31/2013
- No-cost extension end date: 09/30/2013
- Percent complete: 85%

Budget

- Tota project fundin
  - DO s
  -
  - Alga
  - Catalysi p
- Funding
- Funding
- Funding
- Funding
- Funding
- ARR

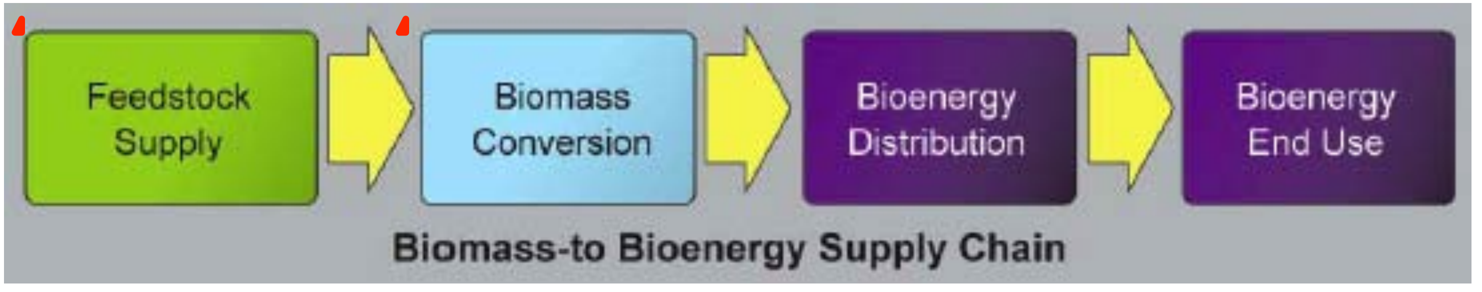
Barriers

- Addressed are Fuel Upgrading & Feedstock Development with feedstock quality by screening and by providing basic cellular biochemical information.

Background

This basic R&D project involves two major goals covering two areas in the Biomass-to-Bioenergy Supply Chain.

- Dr. Polle’s research project supports the first element of feedstock supply.
- Dr. Sanchez-Delgado’s research project supports the second element of biomass conversion.



Project Overview

1. Dr. Sanchez-Delgado's research is in the field of design of new nanostructured catalysts for hydrogenation reactions and study of reaction mechanisms.
2. Dr. Polle's research is in the area of algae strain development with the goal to identify new strains of microalgae for use in biofuels applications. This part of the project was developed in the context of the AFOSR and DOE algae programs.

1A – Approach: Catalysis

1. Catalysis

1.1 Synthesis and characterization of new nanostructured catalysts

- *Develop and apply preparative method(s)*
- *Characterize new catalysts by TEM, XRD, XPS, surface area, metal dispersion.*

Milestones: Hiring and training of 1 postdoc and 5 students (2 PhD and 3 undergrads). Five new catalysts now available and characterized.

1.2 Catalyst screening

- *Screen for catalytic activity in hydrogenation of aromatic compounds representative of fossil fuel components*

Milestones: Setting up multireactor for catalytic testing; results for hydrogenation of aromatics, N-heterocycles and S-heterocycles with new catalysts now available

1.2 Mechanistic studies

- *To understand the reaction mechanisms operating in the catalysis*

Milestones: Novel reaction mechanisms were identified

2A – Catalysis
Technical Accomplishments/ Progress/Results

Tasks	*Status*
1. Hiring personnel	Completed
2. Training of Personnel	Completed
3. Setup the new equipment	Completed
4. Catalysts synthesis (5 catalysts)	Completed
5. Catalyst characterization	Completed
6. Catalyst screening for hydrogenation	Completed
7. Catalyst screening for dehydrogenation	Ongoing
8. Mechanistic studies	Ongoing
9. Project Reporting	On track
10. Dissemination of research results	Ongoing

3A – Catalysis
Relevance

- The accomplishments of this section of the project are significant as fundamental contributions to the advancement of catalytic science, applied to fossil fuel and biodiesel improvement, and to hydrogen storage in organic liquids.

5A. – Catalysis
Future Work

- To complete the work on hydrogenation / dehydrogenation of N-heterocycles catalyzed by ruthenium nanoparticles supported on multi-walled carbon nanotubes, as a method for hydrogen storage in organic liquids.

- To submit three more manuscripts for publication (Rh/MgO, Ru/MgO, Ru/MWCNT)

6A – Catalysis
Summary

- Summarize the key points you wish the audience and reviewers to take away from your presentation in the categories of:

1) Approach: Catalyst design based on metallic nanoparticles on functional (basic) supports promote novel reaction mechanisms that lead to high activity in hydrogenation reactions of potential utility in the manufacture of cleaner fossil fuels, more stable biodiesel, and hydrogen storage in organic liquids.
2) Achievements: Five new catalysts were prepared, characterized, and tested. Reaction mechanisms were investigated.
3) Relevance: the new catalysts are highly active and versatile for hydrogenation of a wide variety of aromatics, of FAMEs and for dehydrogenation of N-heterocycles. Unprecedented reaction mechanisms have been elucidated.
4) Future Work: to use the new knowledge to design further generations of improved catalysts
5) Technology transfer: if the activities achieved reach a high enough level, our catalysts could be of interest to catalysis companies.

7A. Catalysis
Publications, Presentations, and Commercialization

Publications

1. **M. Fang, N. Machalaba and R A. Sánchez-Delgado**,* "Hydrogenation of arenes and N-heteroaromatic compounds over ruthenium nanoparticles on poly(4-vinylpyridine): a versatile catalyst operating by a substrate-dependent dual site mechanism" *Dalton Trans.* **2011,** *40*, 10621–10632.
2. **R. Rahi, M. Fang, A. Ahmed and R. A. Sánchez-Delgado*, "**Hydrogenation of quinolines, alkenes, and biodiesel by palladium nanoparticles supported on magnesium oxide." *Dalton Trans.* **2012**, *41*, 14490-14497.
3. **A. Sánchez, A. Ahmed and R. A. Sánchez-Delgado***, "Hydrogenation of arenes, N-heteroaromatic compounds, and alkenes catalyzed by rhodium nanoparticles supported on magnesium oxide." *ChemCatChem* **2013** (submitted)
4. **M. Fang and R A. Sánchez-Delgado**,* "Ruthenium nanoparticles supported on magnesium oxide: a versatile and recyclable bifunctional solid catalyst for hydrogenation of mono-/poly-cyclic arenes, N-heteroaromatics and S-heteroaromatics" **2013** (manuscript in preparation)
5. **A. Sánchez, M. Fang, D. Vovchok and R. A. Sánchez-Delgado**,* "Hydrogen storage in organic liquids: ruthenium nanoparticles supported on multi-walled carbon nanotubes efficiently catalyze the hydrogenation/dedydrogenation of N-heterocyclic compounds under mild conditions" **2013** (manuscript in preparation).

7A. Catalysis
Publications, Presentations, and Commercialization

Presentations

1. "Mild Catalytic Hydrogenation of Alkenes, Arenes, and Heteroaromatic Compounds by Rhodium Nanoparticles Supported on Magnesium Oxide". **A. Sánchez and R. A. Sánchez-Delgado**, *Gordon Research Conference on Catalysis*, **June 2012**.

2. "Selective Hydrogenation of N-heterocyclic Compounds, Olefins, and Fatty Acid Methyl Esters (FAMEs) by Pd Nanoparticles Immobilized on Basic Supports". **R. Rahi, A. Ahmed and R. A. Sánchez-Delgado,** *Gordon Research Conference on Inorganic Chemistry*, **June 2012**.

3. "Catalytic Hydrogenation in the Manufacture of High Quality Biodiesel", **A. Ahmed, R. Rahi and R. A. Sánchez-Delgado,** 60th Annual Undergraduate Research Symposium (URS), American Chemical Society's New York Section, **May 2012**.

4. "Nanostructured Hydrogenation Catalysts: Novel Reaction Pathways of Relevance to the Manufacture of Cleaner Fuels". **R. A. Sánchez-Delgado**, Invited Talk, *CUNY Nanotech Workshop*, **Nov. 2012**.

5. "Hydrogenation of aromatic compounds by metal nanoparticles on basic supports". **R. Rahi and R. A. Sanchez-Delgado** 241 American Chemical Society National meeting, Anaheim, CA, **March, 2011.**

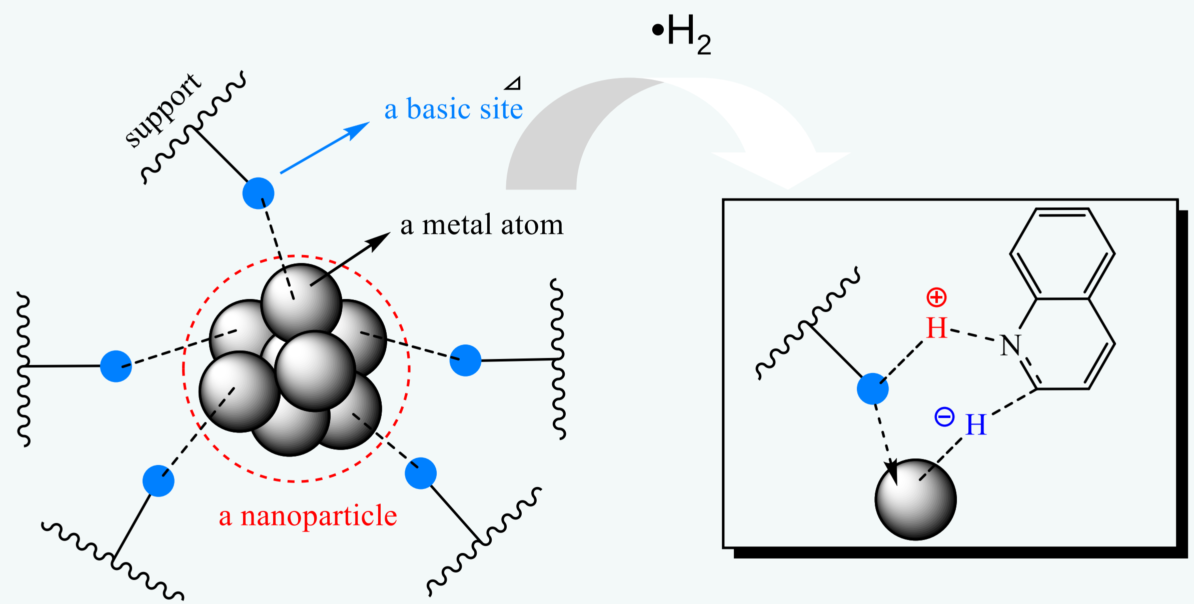
6. "Hydrogenation of quinoline by palladium nanoparticles on MgO". **R. Rahi and R. A. Sanchez-Delgado,** 43rd American Chemical Society Middle Atlantic Regional Meeting, Maryland, **May - June, 2011**.

6. "Ruthenium Nanoparticles Supported on Poly(4-vinylpyridine) as Catalyst for Hydrogenation of Aromatics and Evidence for a Substrate-dependent Dual Site Mechanism". **M. Fang and R. A. Sánchez-Delgado**, 43rd American Chemical Society Middle Atlantic Regional Meeting, Maryland, **May - June, 2011**.

7. "Catalytic Hydrogenation and Related Reactions of Relevance to the Manufacture of Cleaner Fossil Fuels" **R. A. Sánchez-Delgado**, Invited seminar, Columbia University, Earth and Environmental Engineering Department, **Sept. 2011**.

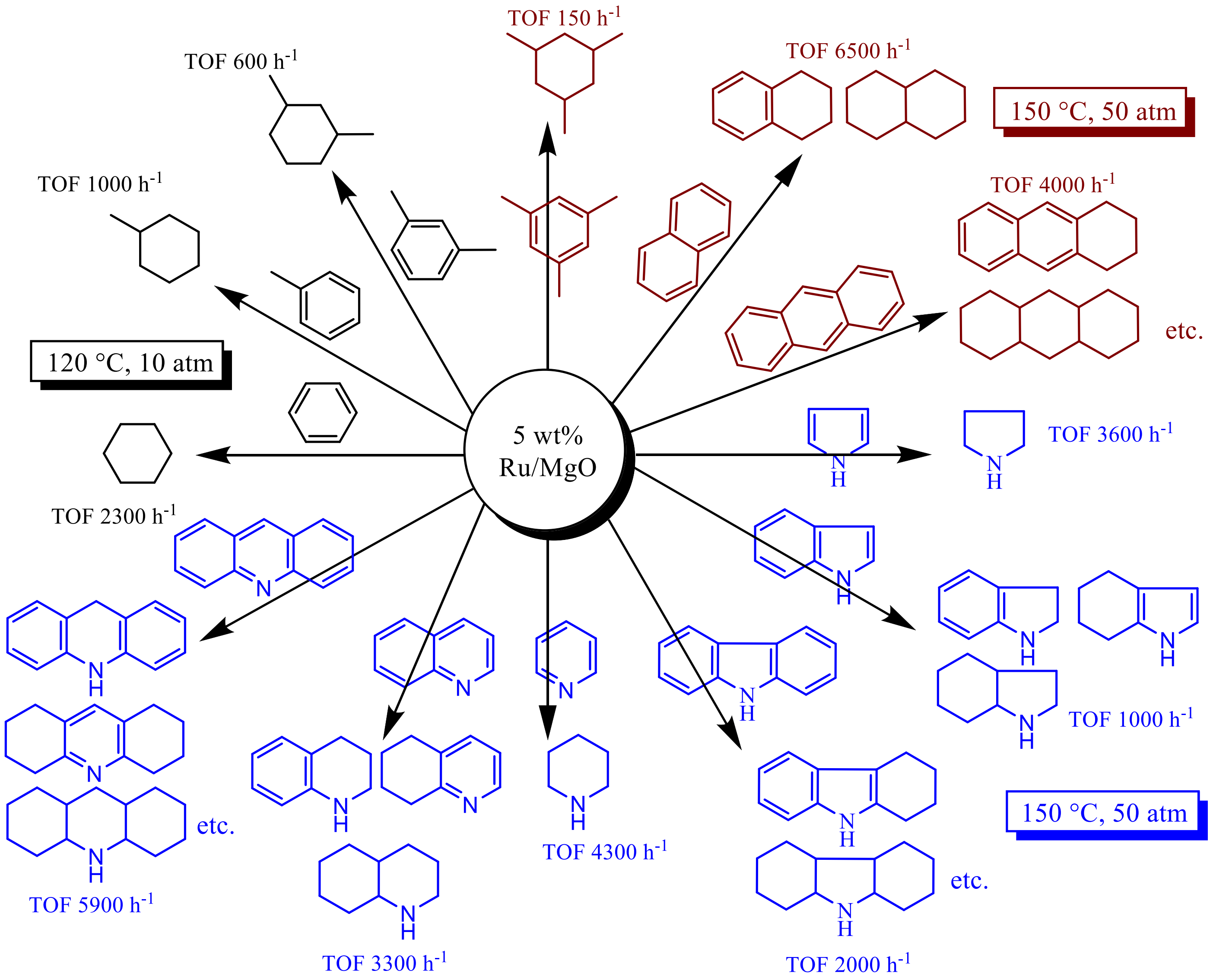
Our general catalyst design

•Nanostructure for heterolytic H_2 activation on solid surfaces



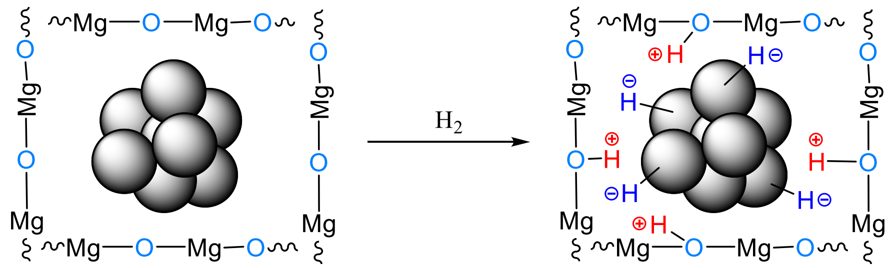
•***Working hypothesis**: A well-defined nanostructure consisting of metallic particles with adjacent basic surface sites will promote heterolytic splitting of H_2 and ionic hydrogenation, thereby avoiding catalyst poisoning and enhancing catalytic activity.*

Versatile hydrogenation catalysts (Ru, Rh)

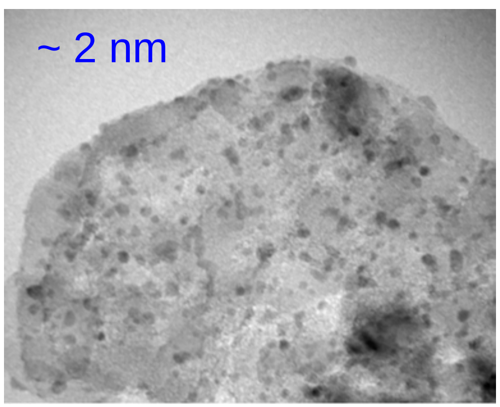


- Very few other MNP catalysts known to hydrogenate N-aromatics, polycyclic aromatics

2nd generation catalysts: M/MgO (M = Ru, Rh, Pd) Synthesis and characterization

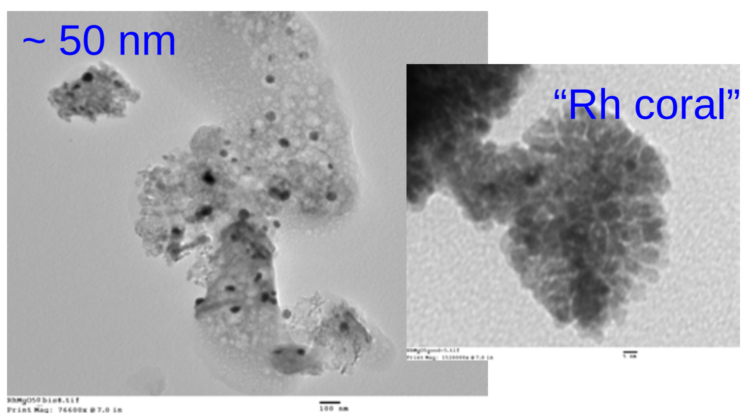


5 wt% Ru/MgO



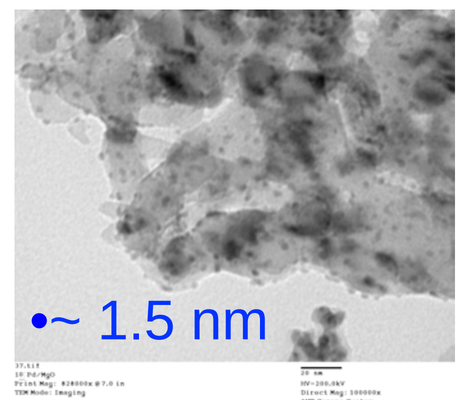
Not yet published

5 wt% Rh/MgO



ChemCatChem, submitted

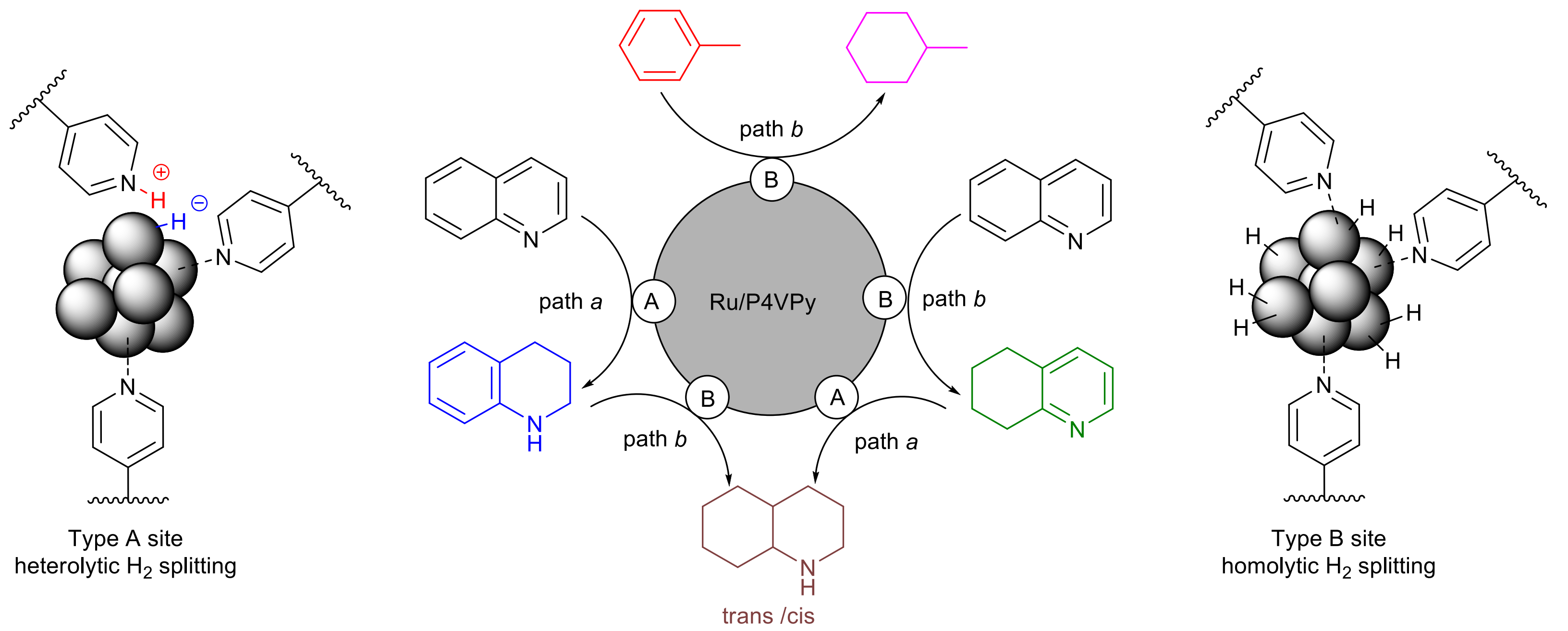
1 wt% Pd/MgO



Dalton 2012

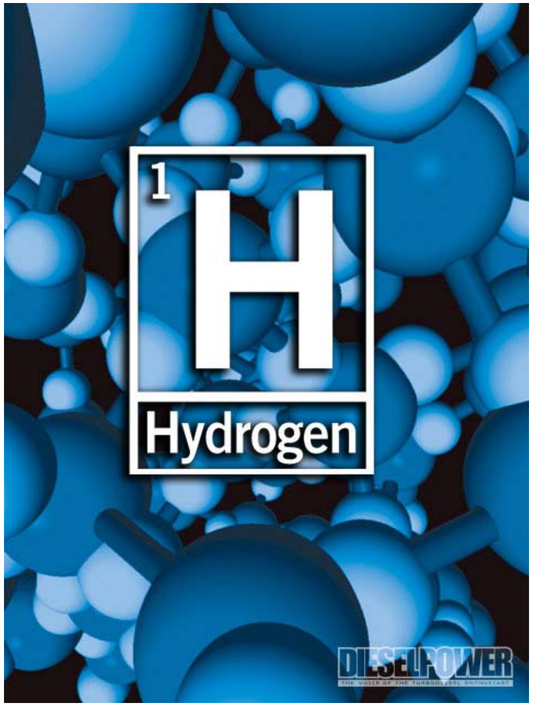
- Also characterized by SEM-EDS, XRD, XPS, BET surface area, H_2 chemisorption

A novel dual-site substrate-dependent hydrogenation mechanism



•Fang, Machalaba, Sánchez-Delgado *Dalton Trans.* **2011**, *40*, 10621–10632.

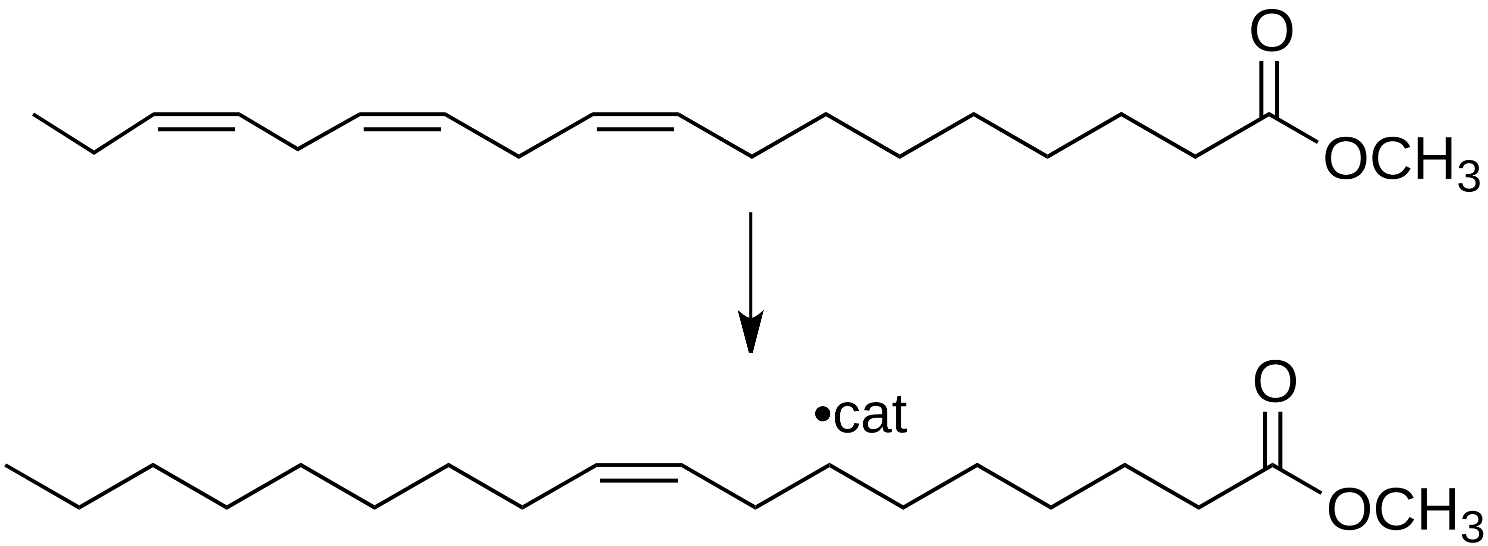
Possible applications of hydrogenation to non-conventional fuels



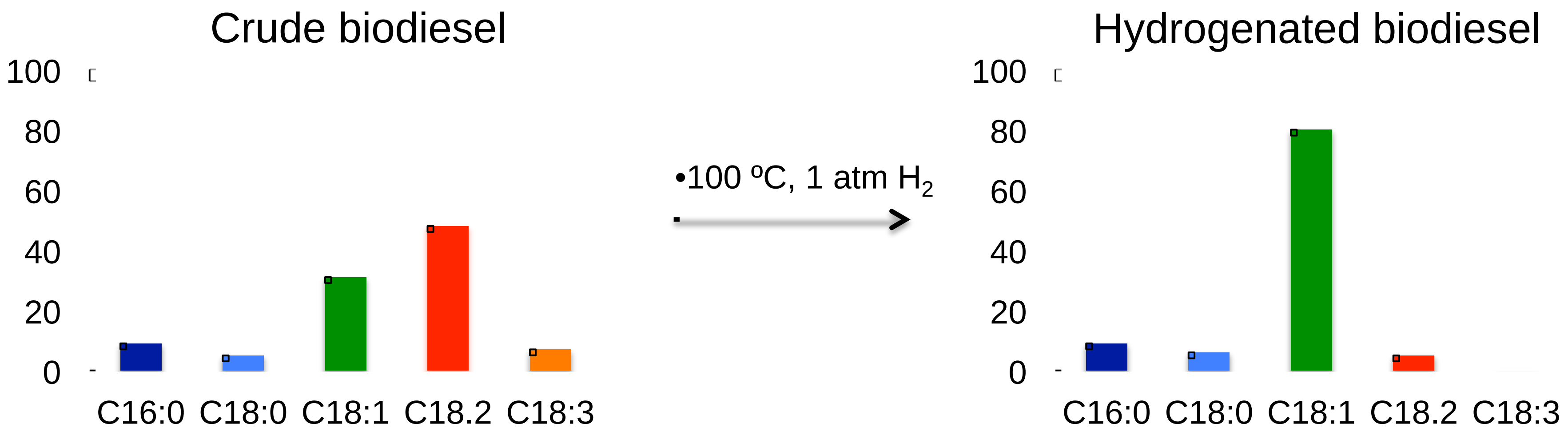
Hydrogenation in Biodiesel Upgrading

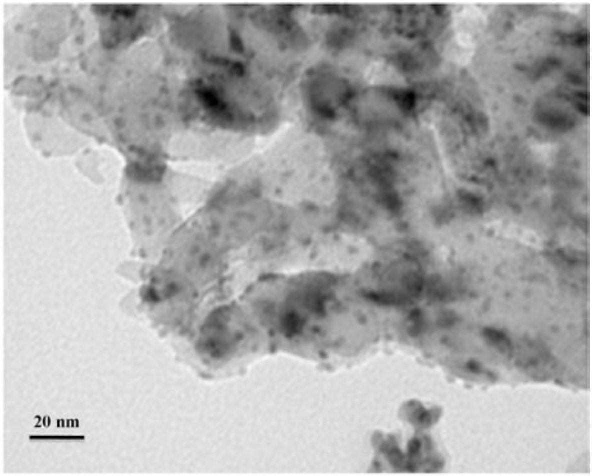
- Biodiesel is inherently unstable to oxidation, ageing (storage) issues

Selective partial hydrogenation enhances fuel properties



Selective hydrogenation of biodiesel using Pd/MgO



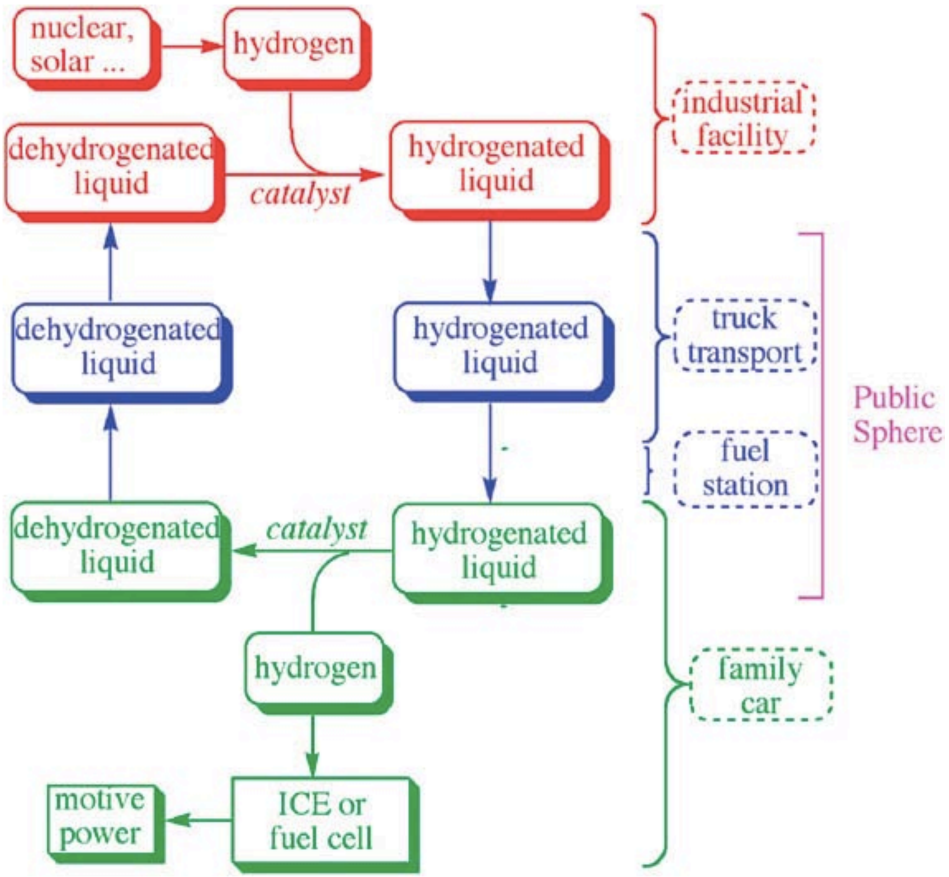


More active than other known catalysts
under extremely mild conditions

Also very active/selective for hydrogenation of quinolines

Rahi, Fang, Ahmed and Sánchez-Delgado, Dalton 2012

Hydrogen storage in organic liquids

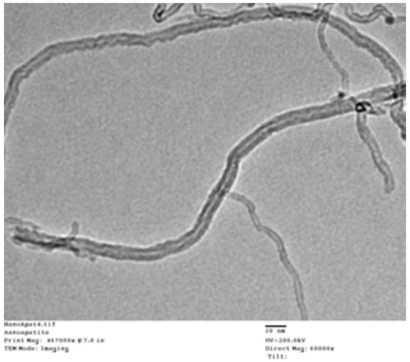


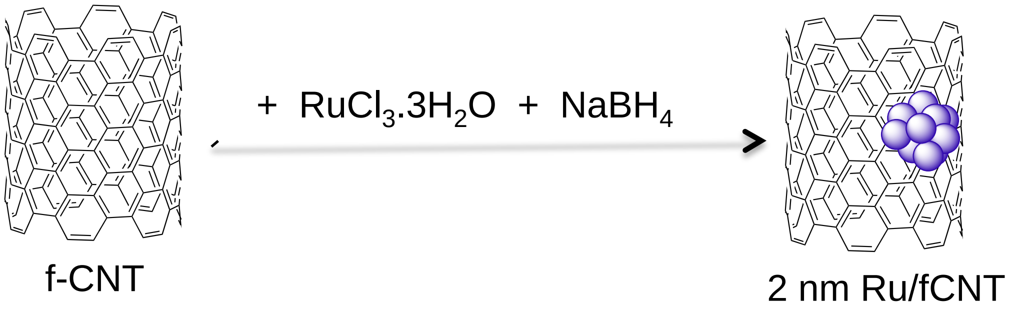
•From: R. H. Crabtree, Energy & Environ. Sci. 2008

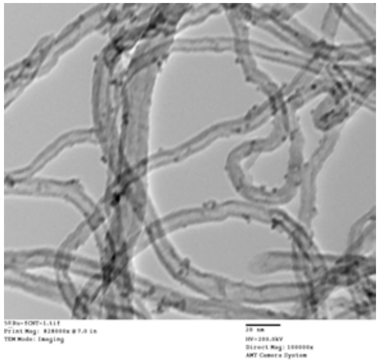
- Requires new catalysts for hydrogenation and dehydrogenation of N-aromatics

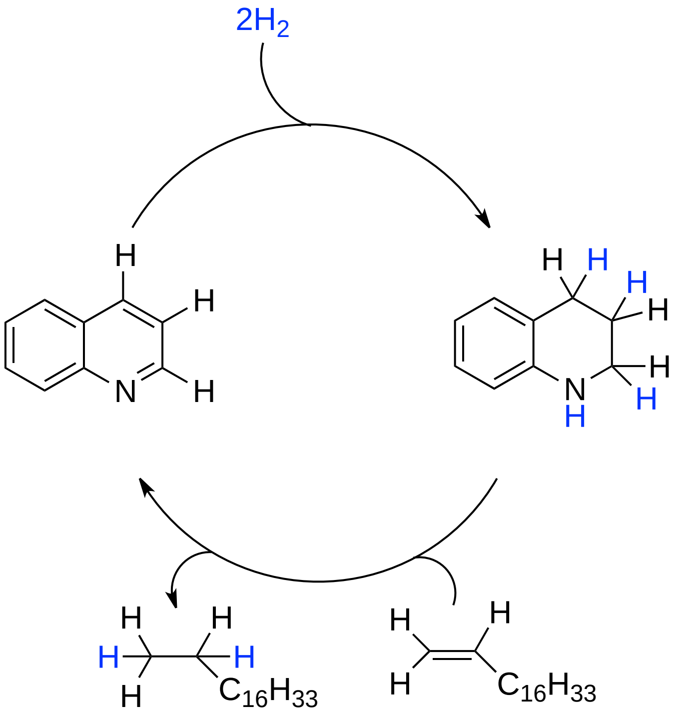
Ru NPs on modified multi-walled carbon nanotubes as catalysts for H_2 storage in liquids

•Sánchez, Fang, Vovchok, Sánchez-Delgado, manuscript in preparation









- We can store H_2 in quinoline
  270 mol H_2 / mol Ru.h
  150 ºC, 10 atm

- And recover it
  66 mol H_2 / mol Ru.h
  150 ºC

New catalyst prepared appears promising for this type of application

2. Project Overview
- Algae Research

- The first aim of the algae research project is the high-throughput screening of recently isolated strains of microalgae for rapid detection of cellular metabolites to be used in biofuels applications.
- In the past a fluorescent dye was used for indirect rapid detection of lipids in algal cells. We aimed to replace the indirect method with a direct rapid detection of cellular lipid content and composition.

1B – Algae Project
Approach

1B.1 Microalgae Biomass Analysis

1B.1.1 Obtain a lipid profile for strains of algae

- *Extract lipids from cells of existing strain collection.*
- *Separate the lipid classes.*
- *Identify the lipid molecules.*

Milestones: Set-up of instrument, hiring and training of personnel.

1B.1.2 Determine the best strains based on lipid class and content

Milestones: Strains screened.

1B.2 Isolate the oil bodies of promising strains and analyze the metabolites/proteins.

- *Fractionate cells of microalgae.*

Milestones: Development of fractionation protocols.

2B – Algae Project
Technical Accomplishments by Task

Tasks	*Status*
1. Hiring personnel	Ongoing
2. Training of Personnel	Ongoing
3. Setup the new equipment	Completed
4. Strain Cultivation	~5,000
5. Metabolite Extraction	>200
6. Biomass Analysis	>10
7. Identification of Promising Strains	>5 strains
8. Isolate oil Bodies from two Microalgae	Ongoing
9. Project Reporting	On track

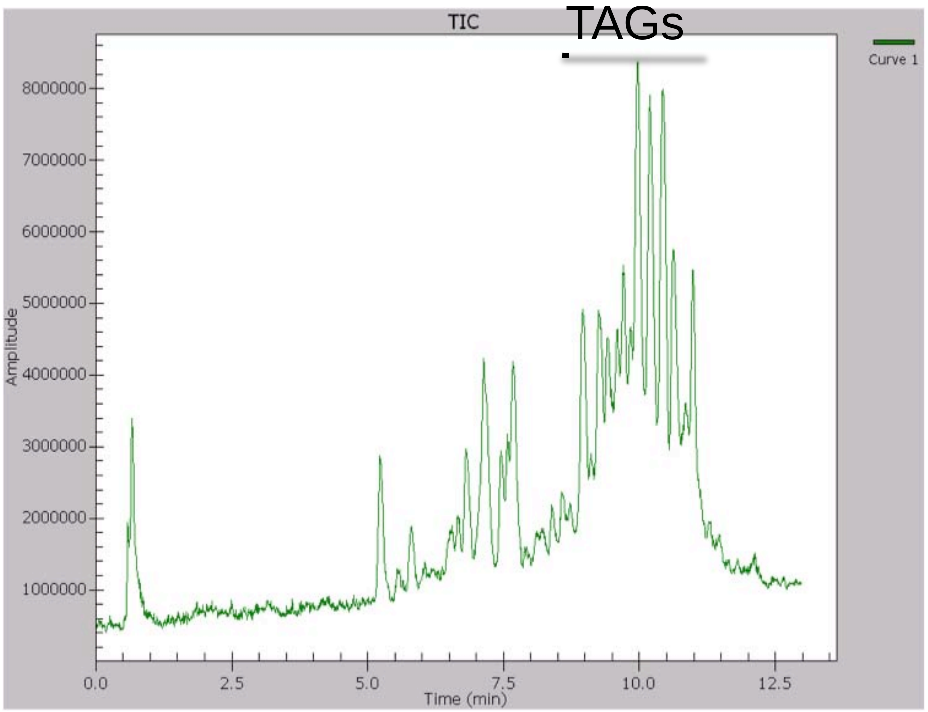
10. Dissemination of research results as posters, various oral presentations at national and international level, and one publication.

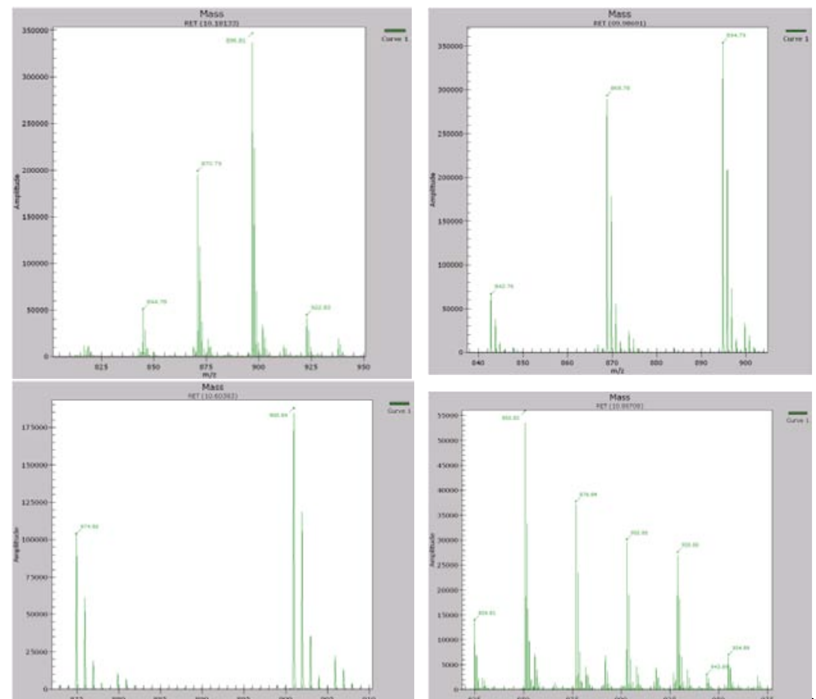
Example Technical Accomplishments Results

Task Identification of a promising algal strain.

The unicellular green alga *Dunaliella salina*

Strain	Neutral Lipids	Polar Lipids	Total Lipids
Dunaliella salina	*15.9%*	*23.7%*	*39.6%*

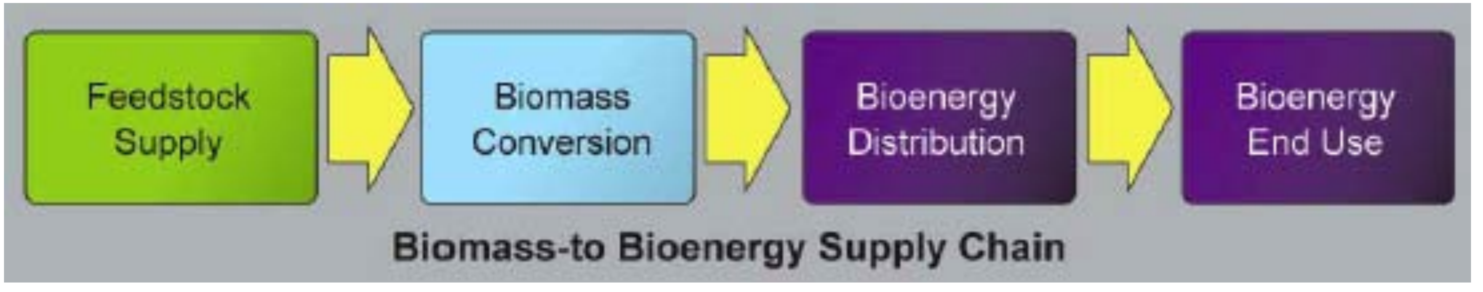




3B – Algae Project
Relevance

Our goal is to enable the production of biofuels.

- This basic R&D project aims at increasing the production of biofuels through identification of superior new strains of microalgae to be used for sustainable, high-quality feedstock production as well as to provide an understanding of the metabolism of the algal cells.



4B – Algae Project
Critical Success Factors

- ***Critical success factors***

  Several algal species identified in our research in the laboratory were successfully scaled up for further analysis in outdoor testbed facilities of collaborating institutions (NAABB project funded by US DOE).

- ***Technical challenge for oil body isolation/analysis***

  Cell walls of many species interfere with extraction of lipids and with isolation of oil bodies.

- ***Connection to other ongoing research***

  This project fits into ongoing collaborations with other institutions within the NAABB consortium.

5B – Algae Project
Future Work

- Continue research on identified platform strains.
- Use results from this project to compare metabolic networks between different types of microalgae.
- Continue to educate students hands-on about systems biology research.

6B - Algae Project

Summary

- Screening using mass spectrometry provides fast information on lipid profiles and lipid contents of microalgae strains.
- Protein profiles of cellular compartments can be obtained, but interpretation of data is hampered by general lack of knowledge on protein functions in organisms. Consequently, a general bottleneck lies in the area of analysis of function of proteins.

Publications and Presentations

Publication:

Hildebrand, M., Abbriano, R.M., Polle, J.E., Traller, J.C., Trentacoste, E.M., Smith, S.R., Davis, A.K. (2013) Metabolic and cellular organization in evolutionarily diverse microalgae as related to biofuels production. Current Opinion in Chemical Biology, in press

Poster:

(2011) Polle J.E.W. et. al. “Lipidomics of the Unicellular Green Alga *Dunaliella salina*.” Joint Genome User Meeting 2011, Walnut Creek, CA, USA

Invited Oral Presentations:

Polle J.E.W., (2011) ”Microalgae strain development for biofuels applications.” 3rd Annual Algae World Summit in May in San Diego, CA.

Polle J.E.W., (2011) ”Identification of novel strains of microalgae for biofuels applications.” First International Conference on Algal Biomass, Biofuels, and Bioproducts in July in St Louis, MO.

Polle J.E.W., (2011) “The Potential of Microalgae for Biofuels Applications: Identification of novel strains of algae.” Hofstra University, Long- Island, NY, USA.

Polle J.E.W., (2012) "Microalgae Biofuels: Strain Selection and Metabolism.” University of Illinois at Urbana-Champaign, IL, USA

Polle J.E.W., (2012) "Microalgae strain development: From cell isolation to cell factories.” Brooklyn College of CUNY, Brooklyn, NY, USA

Polle J.E.W., (2012) "Strain Development of Microalgae: From strain isolation to cell factories.” Conference on Genomics & Systems Biology at NYU Abu Dhabi, Abu Dhabi

Polle J.E.W. (2012) “Isoprenoid metabolism in microalgae: Biosynthesis, regulation, and metabolic sinks.” 2nd Algal BBB, San Diego, CA, USA