2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

6.5.2.2 U.S.-China collaboration-Thermochemical Conversion of Biomass

May 21th, 2013

Principal Investigators: Jonathan Male, Huamin Wang

Technology Area Review: Bio-oil

Organization: PNNL

Goal Statement

- GOAL: Combine and leverage U.S. and Chinese expertise to evaluate, develop, and enable commercially viable processes in thermochemical conversion of biomass to advanced biofuels that mutually benefit both nations

- BETO pathways: Bio-oil and Upgrading Pathways
  Gaseous Intermediates Pathways

Quad Chart Overview

Timeline

- Project start: August 2008
- Project end: September 2013
- 90% complete

Barriers

- Barriers addressed:
  - *Gt-G. Fuel Synthesis and Upgrading*
  - *Tt-G. Fuel Synthesis and Upgrading*
  - *At-C. Inaccessibility and Unavailability of Data*

Budget

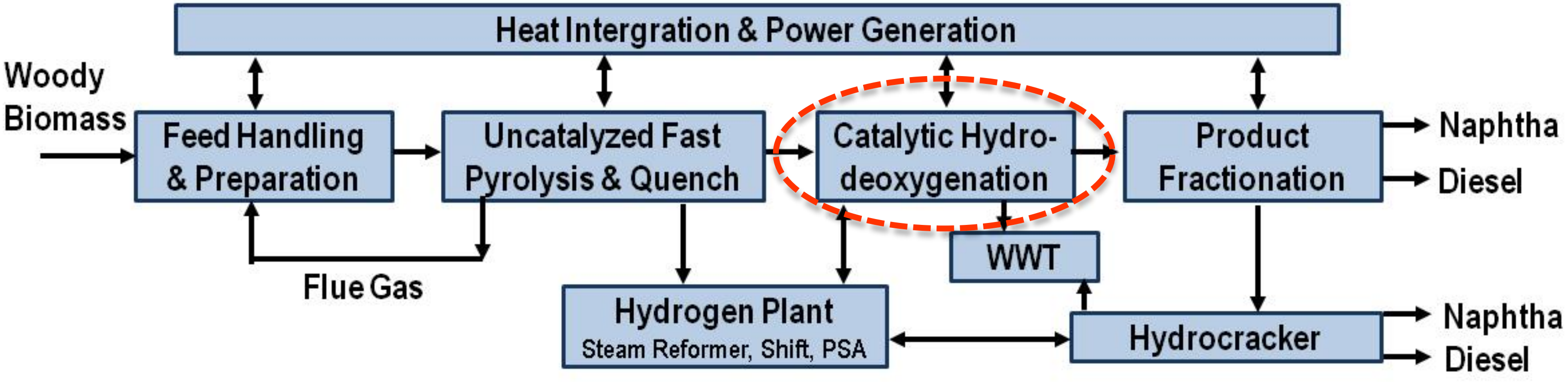
- Total Project funding $1,100 k
- Funding in FY11
  $100 k
- Funding in FY12
  $100 k
- Funding for FY13
  $0 k
- Average annual funding: $183 k/yr

Partners

- Collaborations:
  - Dalian Institute of Chemical Physics (DICP)
  - China National Offshore Oil Corporation (CNOOC)
  - Qingdao Institute of Bioenergy and Bioprocess Technology (QIBEBT)
  - Tsinghua University (Tsinghua)

Project Overview

- Collaboration of U.S. and China began in FY2008 with the signing of an MOU
- The program expanded with a collaboration of PNNL with CNOOC and DICP in 2009: **Gaseous Intermediates Pathways**
  - Techno-economic analysis for conversion routes to advanced biofuels and compare scenarios in the U.S. to those in China
  - Detailed understanding the critical catalyst bottle-neck for the thermochemical conversion of biomass to biofuels: **catalysts for syngas to mixed alcohols**
- The program further expanded with a collaboration of PNNL with QIBEBT and Tsinghua in 2012: **Bio-oil Pathways**
  - Transition to a second critical catalyst bottle-neck: **catalytic hydrotreating of biomass fast pyrolysis oil**
  - Detailed understanding of bio-oil hydrotreating catalysts



1 - Approach

Technical Approaches

Project with CNOOC and DICP

- Use U.S. and Chinese technology, logistics, and costing for techno-economic analysis to enable comparisons and guides decision making
- Develop detailed understanding of novel fuel synthesis catalysts developed at DICP: catalyst characterization, bench scale testing, and computational modeling

Project with QIBEBT and Tsinghua

- Complete a literature study to help the development of strategy to address the second critical catalyst bottle-neck
- Develop detailed understanding of bio-oil hydrotreating catalysts: study deactivation mechanism at bench scale, and examine functional requirements of catalysts with improved stability

Management Approaches

- Periodic communications and data exchanges to coordinate Chinese and EERE/BETO international team efforts (telephone conferences, emails and monthly reporting)
- Milestones and deliverables established in the project management plan

2 - Technical Accomplishments

Outline of key accomplishments to be discussed:

Project with CNOOC and DICP

- Developed three preliminary techno-economic analyses: distributed pyrolysis oil production fed to a centralized upgrading system to gasoline and diesel; landfill gas to gasoline via oxidative coupling of methane; syngas conversion to ethanol
- Effect of support and additives on the mixed higher alcohols synthesis from syngas over Co catalysts: a combined theoretical and experimental study

Project with QIBEBT and Tsinghua

- A literature study: recent advances in hydrotreating of pyrolysis bio-oil and its oxygen-containing model compounds
- Deactivation mechanism of bio-oil hydrotreating catalysts: detailed characterization and computational modeling

2 – Technical Progress:

Milestone	Planned Completion Date	Completion
Complete third TEA scenario with Chinese inputs and compare to U.S. scenarios	Sep 2012	✓
Summarize the preliminary understanding of the mechanism of the coke formation on deactivated bio-oil hydrotreating catalysts	Dec 2012	✓
Create a draft manuscript on catalyst deactivation mechanisms for subsequent submission to a peer reviewed journal	Feb 2013	✓
Fourth techno-economic analysis technology pathway and U.S. - Chinese scenario comparison report	Mar 2013	✓
Identify at least one deactivation mode of an upgrading catalyst and the functional requirement of bio-oil hydrotreating catalysts which will lead to a more stable catalyst	Jun 2013	60%
Complete annual progress report	Sep 2013	On schedule

2 - Technical Accomplishments
Techno-Economic Analysis

High level analysis of interest to BETO and China partners (using public literature and standard BETO assumptions for U.S. costs and China partner assumptions for China costs)

Case 1: Distributed Processing - 3x2000 tonne/day pyrolysis units feeding a centralized gasifier (reported in previous peer review)

- Syngas conversion to mixed alcohols based on 2007 TC Design case
- Costs for transporting pyrolysis treated as a pyrolysis oil cost sensitivity
- Design case alcohol catalyst performance suggests $3/gal ethanol (2007$) possible – **Reviewed in 2011**

Case 2: Distributed pyrolysis to consider plant scale and transportation costs to a central upgrading site

- Distributed system analysis using China transportation & biomass prices
    - Smaller scale distributed systems (5, 50, **200** MT/day) feeding a central upgrader appear cost competitive with a **4000** MT/day pyrolysis and upgrading unit (fuel production cost 4.7 Yuan/L, when biomass transportation unit cost = 4 Yuan/dry MT/km)

2 - Technical Accomplishments
Techno-Economic Analysis

Case 3: Conversion of landfill gas (LFG) to gasoline

- LFG generated by microbial action on landfill organic matter
- LFG an inexpensive biogenic methane source
- Oxidative coupling of methane (OCM) in the LFG converts the gas to light olefins which are then converted to gasoline via oligomerizaton
- Baseline case at 10 mmscfd (0.27 million Nm^3/d) LFG
  - ~$6/gallon (US 2011$) gasoline (~10 Yuan/L China 2007 Yuan)
- Capital reduction (e.g. lower OCM temperature, improved oligomerization catalyst) reduces gasoline price 3 – 7%

Case 4: Syngas fermentation to ethanol – 2000 tonne/day wood

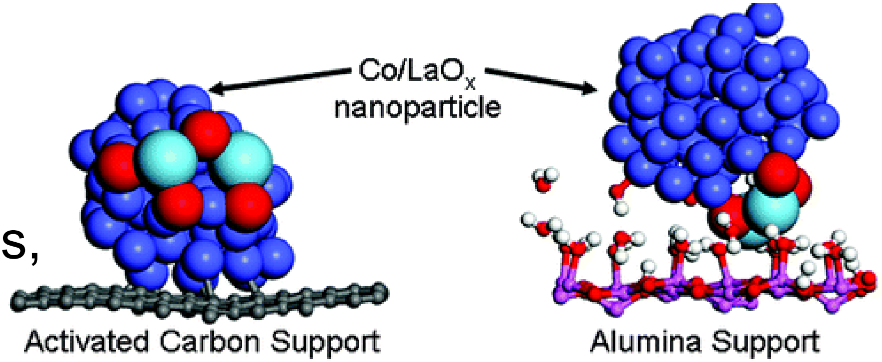
- Two bounding scenarios:
  - Tar cracker: lower capital, higher BTU fermenter offgas
  - Tar reformer: higher capital, more CO to fermenter => improves yield
- Results suggest ethanol costs of $2-4/gallon (2011 USD) or 3-5 Yuan/L (2007 Yuan)
- Research needed to better understand/optimized CO & H_2 conversion

2 - Technical Accomplishments
Unique Co-La-Zr fuel synthesis catalyst

Combination of *in situ* and *ex situ* catalysis characterization, reactivity studies, and theoretical calculations presents a detailed picture of the role of La_2O_3 doping on Co catalysts

Catalysts	CO Conv. (%)	ROH Select. (%)	Alcohol distribution (%)		
			C1	C2-C5	C3
Co/AC	29	13.2	23	77	0
Co-La/AC	58	20.4	11	57	32
Co-La-Zr/AC	55	21.7	14	51	35
Co-La-Zr/Al_2O_3	13	4.5	22	76	2

- Addition of lanthanum leads to an increase of the alcohol selectivity by promoting Co_2C formation.
- Activated carbon (AC) supports promote Co_2C formation, whereas oxides supports, such as alumina, inhibit it.

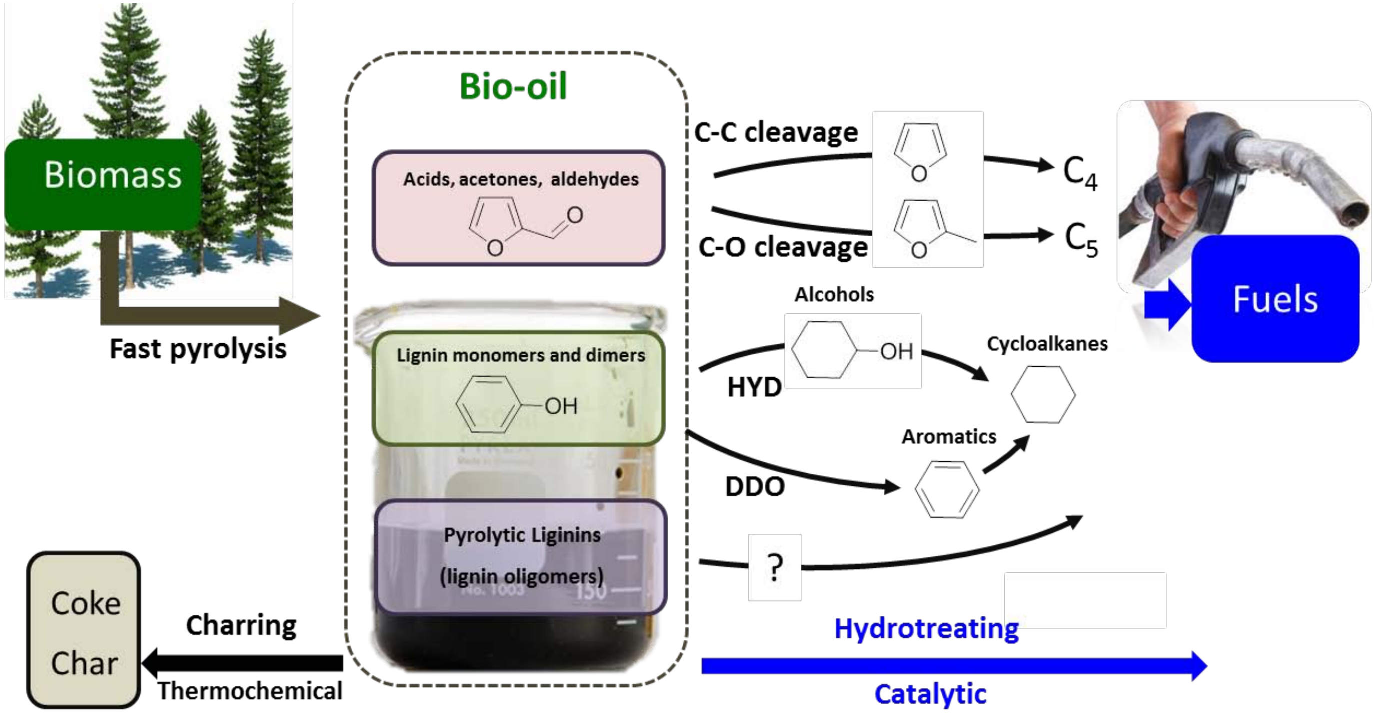


- Increasing the Co_2C/Co° ratio in the catalyst enhances selectivity towards higher alcohols from syngas

Lebarbier, V.M.; Mei D.; et al J Phys. Chem. C. 2011,115,17440

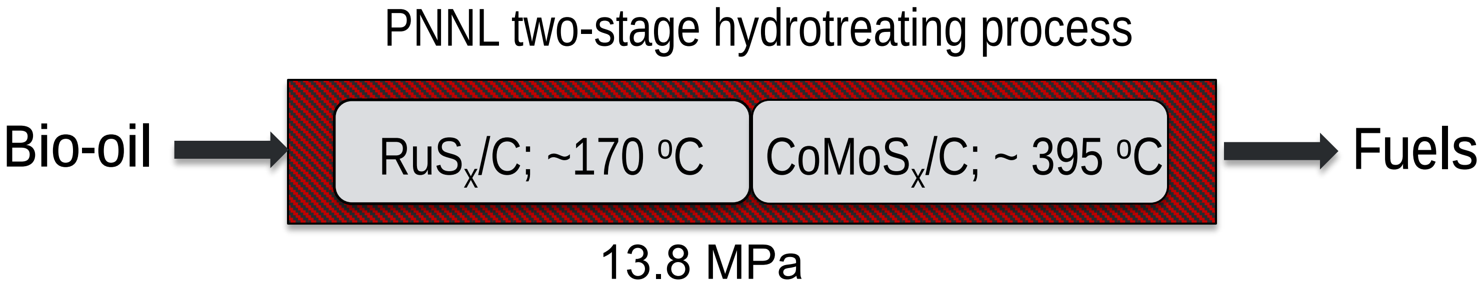
2 - Technical Accomplishments
Transition to bio-oil hydrotreating

- A literature study: recent advances in hydrotreating of pyrolysis bio-oil and its oxygen-containing model compounds, was recently published as a review paper in ACS Catalysis
- The deactivation of the catalysts still remains a big challenge and there is lack of knowledge on the critical aspects that impact the stability of the hydrotreating catalysts



Wang, H.; Male, J.; Wang, Y. ACS Catalysis, 2013, *3,* 1047-1070.

2 - Technical Accomplishments
Deactivation of Bio-oil Upgrading Catalysts



PNNL two-stage hydrotreating process

Bio-oil → RuS_x/C; ~170 °C | $CoMoS_x/C$; ~ 395 °C → Fuels

13.8 MPa

- Loss of catalyst activity

TOS (h)	Oil Yield (g/g dry feed)	H_2 consumption (L/L feed)	Fuel products		
			O (Wt.%)	H/C (dry)	Density (g/ml)
24-50	0.40	444	0.7	1.59	0.86
66-82	0.43	342	2.1	1.47	0.91

- Deactivation of RuS_x/C led to unstablized intermediate, which formed char and then caused reactor plugging over a <100 h test
- $CoMoS_x/C$ have limited catalyst lifetime and exhibited deactivation over a <100 h test

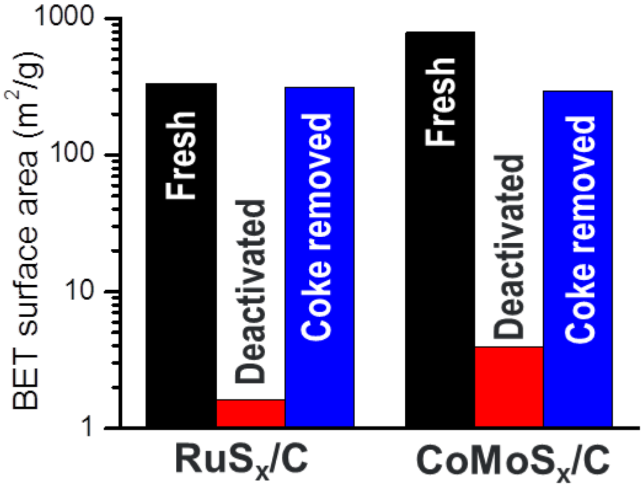
Elliott, D.; et al Energy Fuels 2012, 26, 3891

2 - Technical Accomplishments
Deactivation of Bio-oil Upgrading Catalysts

Deactivation Mode: Severe coke formation and encapsulation of catalyst

Loss of surface area and pore volume

Recovery by coke removal

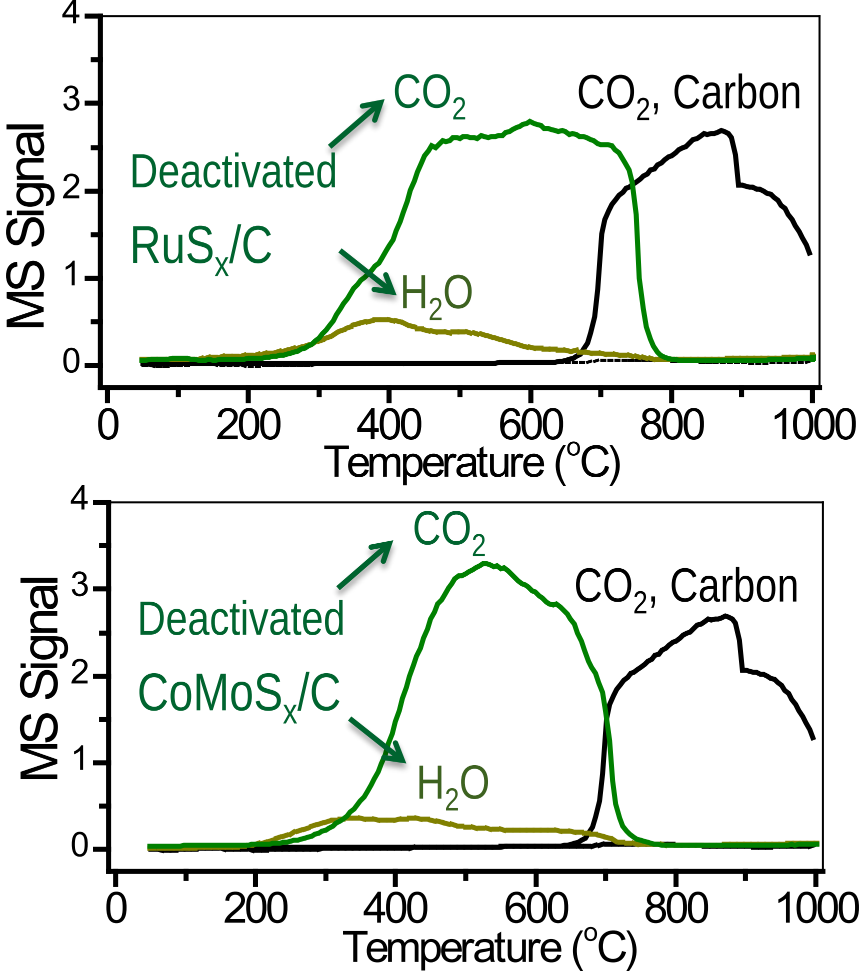


Pyroprobe-GC/MS and XPS:

RuS_x/C: High molecular weight fraction of bio-oil formed by repolymerization

$CoMoS_x/C$: High MW fraction and polyaromatic coke formed by aromatization

TGA-MS: combustion of coke at 300-600 °C

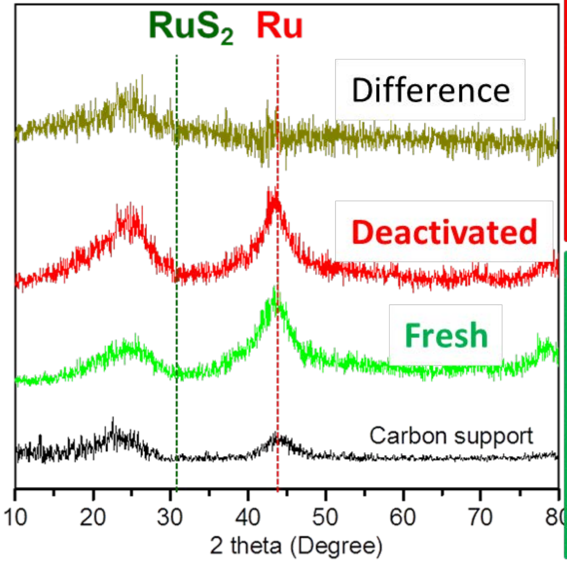


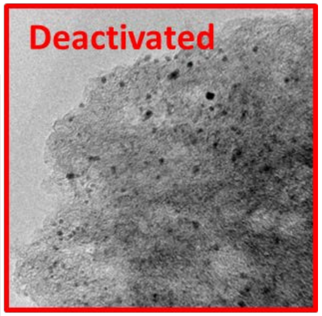
Deactivation of Bio-oil Upgrading Catalysts

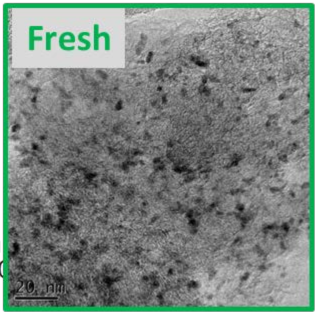
Deactivation Mode: Structural change of CoMoS active phase

RuS_x/C did not show sintering of Ru species

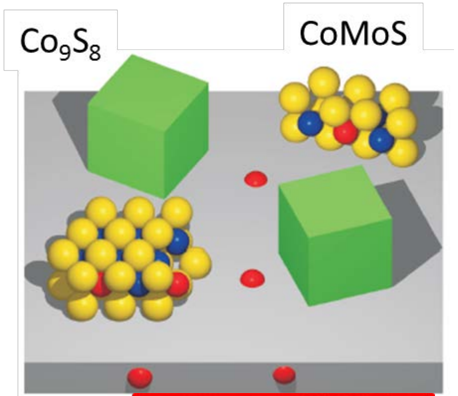
XRD and TEM



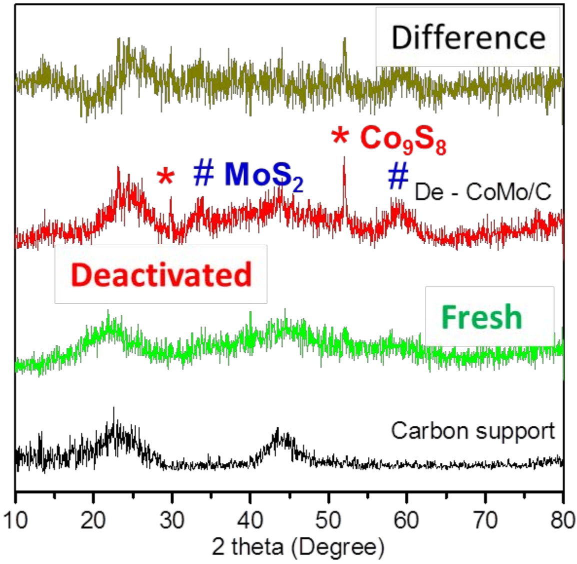


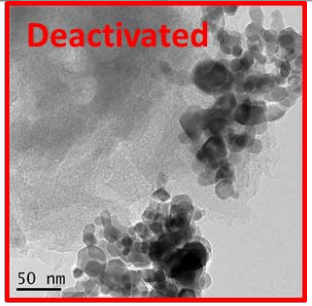


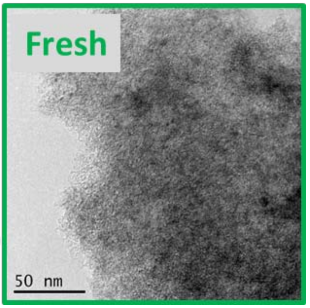
$CoMoS_x/C$ showed segregation of Co from CoMoS active phase and sintering of Co_9S_8.



XRD and TEM







2 - Technical Accomplishments

Deactivation of Bio-oil Upgrading Catalysts

Deactivation Mode: Possible active site poison by inorganic species

- Increase of inorganic content on the deactivated catalysts
- Inorganics might deposit on active sites, causing deactivation
- Sources of inorganics: biomass; heating sand during Fast Pyrolysis; steel reactor

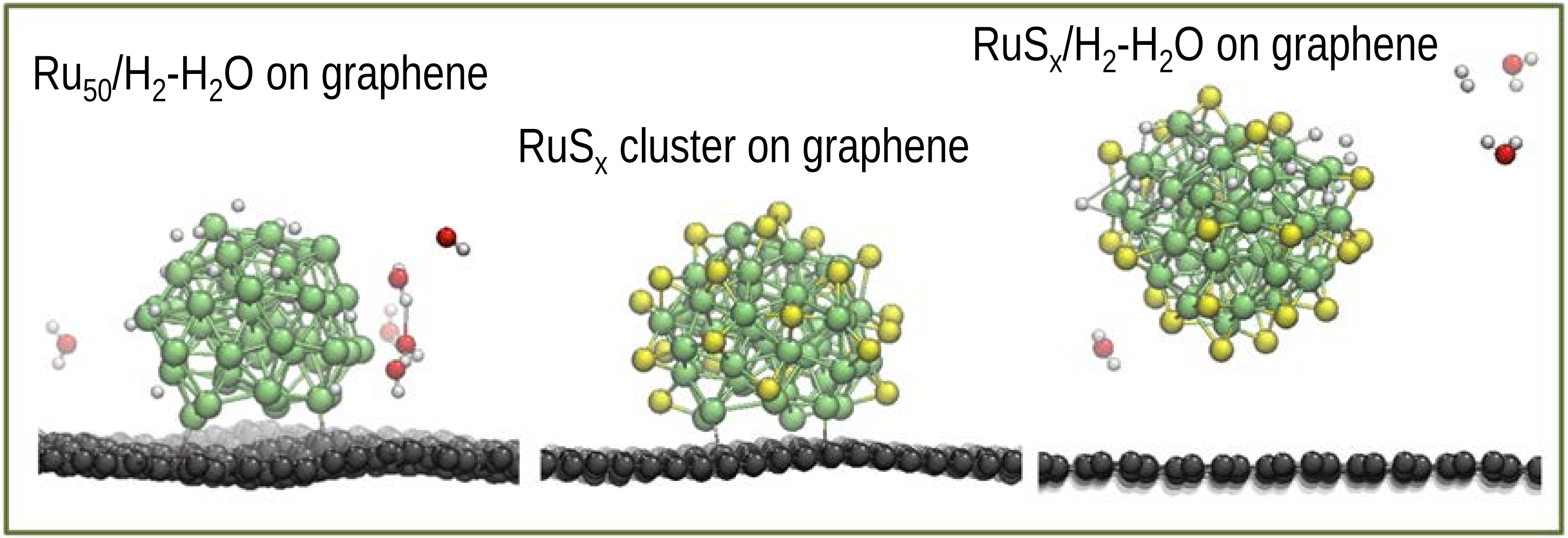
Element*	**RuS_x/C**		**$CoMoS_x/C$**		**Bio-oil**	**317 SS**
	Fresh	Deactivated**	Fresh	Deactivated**		
Cr	-	-	-	389	-	18-20%
Fe	82	289	206	4594	66	Balance
Ni	-	-	-	238	-	11-15%
Al	81	1224	-	5729	38	
Si	285	5781	2083	7189	655	
K	1535	460	303	987	31	
Ca	526	1144	279	902	36	

* By ICP-OES; ** Nominalized to fresh sample

2 - Technical Accomplishments
Deactivation of Bio-oil Upgrading Catalysts

Deactivation Mode: Possible migration of active metals

- Observation of Ru in the stabilized bio-oil after stage I hydrogenation
- *Ab Initio* molecular dynamics simulations have shown that 1nm Ru_{50} nanoparticles are stable on graphene at T = 150 °C in the presence of hydrogen and water but sulfided Ru_{50} clusters are not



3 - Relevance

- Brings together Chinese and U.S. expertise to better understand biomass thermochemical conversion to fuels
- Actively supports thermochemical conversion to drop-in biofuels 2017 targets
- Supports the Memorandum of Understanding (MOU) between U.S. and China
- Supports the President's Blueprint For a Secure Energy Future – The U.S. working with international partner to promote the benefits of sustainable modern bioenergy

MYPP Barriers Addressed:

- *Gt-G. Fuel Synthesis and Upgrading* (more robust mixed alcohol synthesis catalysts)
- *Tt-G. Fuel Synthesis and upgrading* (hydroprocessing catalysts with long steady-state operability)
- *At-C. Inaccessibility and Unavailability of Data*

MYPP Tasks supported:

- R 3.6.3.2.2 - Develop cleanup & conditioning processes (upgrading and stabilizing)
- R 3.6.3.3.1 Develop gasification to other fuels
- R 3.6.4.1 Develop catalyst technologies

Applications of the expected outputs from this project:

- Developing detailed understanding of fuel synthesis and upgrading catalysts to enable and reduce risks on a pathway to commercial viability
- Helps meet the goals of the U.S. – China Renewable Energy Partnership

4 - Critical Success Factors

Critical success factors

- Obtaining techno-economic analysis of biofuels production outside the U.S.
- Detailed understanding of bio-oil hydrotreating catalysts, especially deactivation mechanisms
- Detailed understanding of fuel synthesis catalysts and demonstration of improved catalysts with ability to selectively produce higher alcohols
- Accelerating the performance of biofuels catalysts through modeling

Top potential challenges

- Simultaneously meeting Chinese and U.S. technical goals – continued emphasis of techno-economic targets
- Effective communication and integration with international teams – continued engagement and exchange

Upon success of project

- Potential to increase yields of higher alcohols and drop-in biofuels
- Potential to support the development of bio-oil hydrotreating catalysts with improved stability
- Helps meet the goals of the U.S. – China Renewable Energy Partnership

5 - Future Work

Project with CNOOC and DICP

- Continue to exchange performance and logistics data between U.S./China researchers

Project with QIBEBT and Tsinghua University

ML, DL or Go/No Go	Description	FY13 Q3	FY13 Q4	FY14 Q1	FY14 Q2	FY14 Q3	FY14 Q4
ML	Complete deactivation mechanism study	🟩					
DL	Annual Report		🟩				
ML	Characterization of bifunctional HDO catalysts from China			🟩	🟩		
ML	Evaluation of catalysts from China by bio-oil hydrotreating					🟩	🟩
ML	Computational modeling of active sites of bifunctional catalysts			🟩	🟩		
ML	Techno-economic analysis on bio-oil pathways between US/China					🟩	🟩

Summary

Techno-Economic Analysis combined U.S. and Chinese inputs

Comprehensive understanding of critical catalysts for biomass thermochemical conversion using both experimental and theoretical approach

- Role of La_2O_3 doping on Co catalysts for synthesis of higher alcohols from syngas:
- Deactivation mechanism of bio-oil hydrotreating catalysts

Addresses Technical Barriers: *Gt-G, Tt-G, At-C*

Critical Success Factors

- TEA of biofuels production outside the U.S.
- Detailed understanding critical catalysts
- Combined experimental and theoretical approach

Future Work

- Complete bio-oil hydrotreating catalyst deactivation mechanism study
- Characterization and evaluation of bifunctional catalysts from China
- Techno-economic analysis on bio-oil pathways between US/China

Acknowledgements

- U.S. Department of Energy, Bioenergy Technologies Office: Alison Goss Eng, Sheila Moynihan, and Paul Grabowski
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- China National Energy Administration
- Qingdao Institute of Bioenergy and Bioprocess Technology (QIBEBT), Tsinghua University, China National Offshore Oil Corporation (CNOOC), Dalian Institute of Chemical Physics (DICP).
- U.S. –China MOU for Biofuels Development: Michael Wang (ANL), William Wallace (NREL), Christopher Wright (INL), Erin Webb (ORNL)
- PNNL Thermochemical Collaboration team with China: Yong Wang, Huamin Wang, Yunhua Zhu, Sue Jones, Roger Rousseau, Corinne Valkenburg, Vanessa Lebarbier, Donghai Mei.

Responses to Previous Reviewers' Comments

- Reviewers: The CNOOC work is less clear why the focus on the higher alcohols instead of direct hydrocarbons.
- Response: Within the CNOOC, DICP project the fuel synthesis catalyst was initially designed by DICP and makes higher alcohols than ethanol which was seen as interesting and worthy of understanding in order to enable control of the production of alcohols. In China the current biomass research and development focus is on ethanol production while the U.S. is looking to fulfill ethanol's promise and gain traction on future infrastructure compatible fuels. Understanding the DICP catalyst enables near term goals on fundamental knowledge of catalysts, co-catalysts and supports to be disseminated to help ethanol production. We are cognizant that molecules with >1 carbon-carbon bond already assembled have potential benefits as intermediates for infrastructure compatible blend stocks.
- Reviewers: The IP and commercialization concerns are potentially significant.
- Response: In the CNOOC, DICP project, the work is fundamental in nature and will be available for dissemination, in fact a manuscript has just been submitted to the Journal of Physical Chemistry. As the project becomes more engaged in commercialization, as pointed out by the reviewers, intellectual property plans will have to be developed. Currently there is a memorandum of understanding in place between CNOOC and PNNL and discussions have been held on clarification of the pathways forward regarding intellectual property.
- Reviewers: This distributed pyrolysis model needs to be better understood from a techno-economic standpoint to see if it is truly worth pursuing.
- Response: The reviewers make an excellent point about the scaling and distribution of pyrolysis operations and the benefits and trade-offs with more centralized versus distributed scenarios. The Biomass Program and, in a smaller capacity, this project, hope to move forward on the techno-economic analysis and the sensitivity analysis of the different logistic scenarios in the coming years.

Publications, Presentations, and Commercialization

Publications

- Effects of La_2O_3 on the mixed higher alcohols synthesis from syngas over Co catalysts: A combined theoretical and experimental study. Lebarbier, V. M.; Mei, D.; Kim. D. H.; Anderson, A.; Male, J. L., Holladay, J. E.; Rousseau, R.; Wang, Y. *J. Phys. Chem. C.* **2011,** *115*, 17440.
- Recent advances in hydrotreating of pyrolysis bio-oil and its oxygen-containing model compounds. Wang, H.; Male, J.; Wang, Y. *ACS Catalysis*, **2013**, 3, 1047-1070.
- Characterization of deactivated catalysts for bio-oil hydrotreating. Wang, H.; Male, J.; Wang, Y. *manuscript in preparation*.

Publications, Presentations, and Commercialization

Presentations

Characterization of Fuel Synthesis Catalysts for the Production of Higher Alcohols J.L. Male, 2nd Sino-U.S. Biofuels Forum, Idaho Falls, September 16, 2011.

Theoretical studies of higher alcohol synthesis from biomass derived syngas by modified Fischer-Tropsch catalysts. Roger Rousseau. CPMD2011: Extending the limits of Ab initio Molecular Dynamics Simulations for Chemistry, Materials Science and Biophysics. September 5-9, 2011. Barcelona, Spain.

Higher Alcohols Synthesis over Supported Cobalt Catalysts. Lebarbier, V. M. C.; Rousseau, R. J.; Kim, D. H.; Andersen, A.; Mei, D.; Wang, Y. 22nd North American Catalysis Meeting, Detroit, MI June 5-10, 2011.

Presentation given by Roger Rousseau. China –US Workshop on Frontiers in Chemical Physics and Interfacial Chemistry, June 1-2, 2011. DICP, Dalian, China.

Theoretical studies of higher alcohol synthesis from biomass derived syngas by modified Fischer-Tropsch catalysts. Roger Rousseau. Thermodynamics and Kinetics of Surfaces and Interfaces from Simulations Workshop. June 22-24, 2011. Thomas Young Center, London England.