2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Bio-oil Upgrading with Novel Low Cost Catalysts – Catalyst Development with Synergistic Evaluation

WBS #: 3.2.2.28 & 3.2.2.29

May 21, 2013

Bio-Oil Technology Area Review

(DOE Manager: Melissa Klembara)

PI: Jae-Soon Choi, Oak Ridge National Laboratory

PI: Alan Zacher, Pacific Northwest National Laboratory

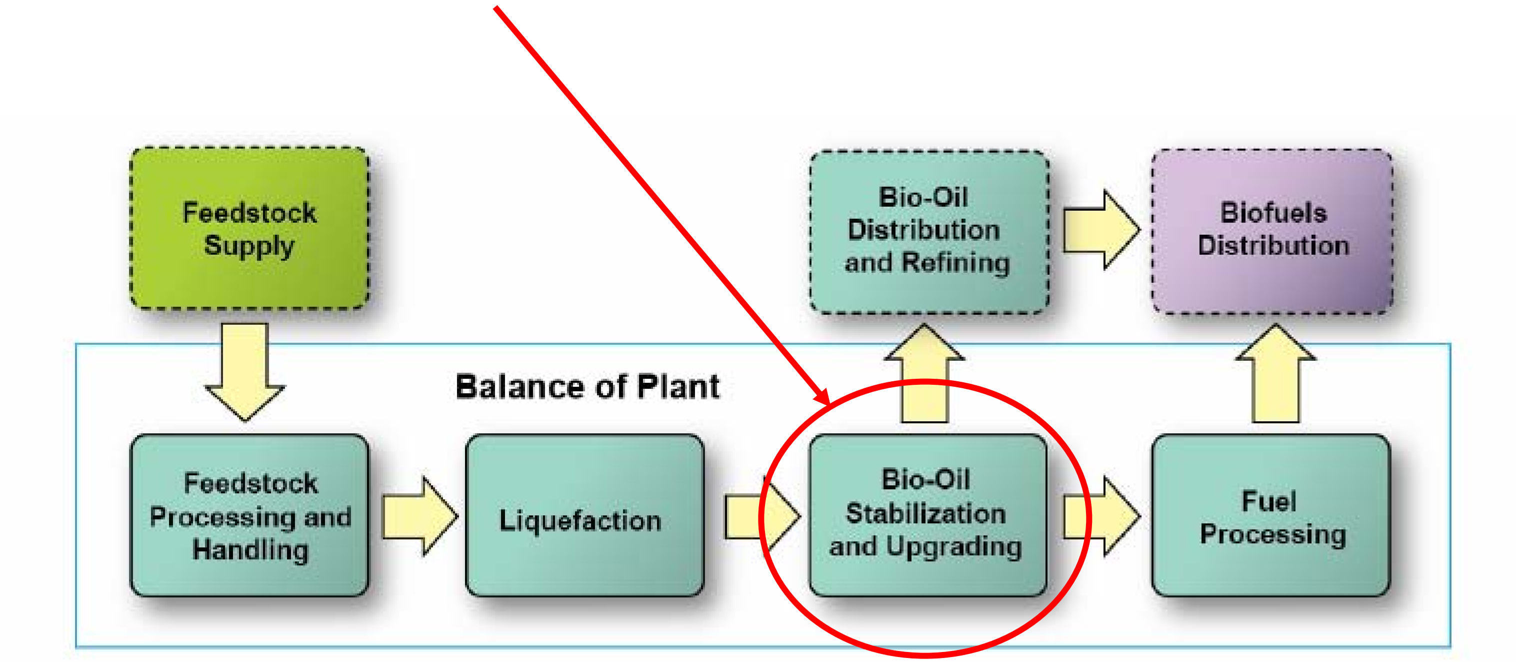
Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE U.S. DEPARTMENT OF ENERGY

Goal Statement

- **Develop novel catalysts for bio-oil hydroprocessing based on catalytic materials that are inexpensive, active, selective, and durable**



Bio-oil pathways route for biomass to biofuels

Bioenergy Technologies Multi-Year Program Plan, November 2012.

Project Quad Chart Overview

Timeline

- Project start date: October 1, 2012
- Project end date: September 30, 2015
- Percent complete: 17%

Budget

	FY12	FY13
ORNL	$0	$400k
PNNL	$0	$100k

Barriers

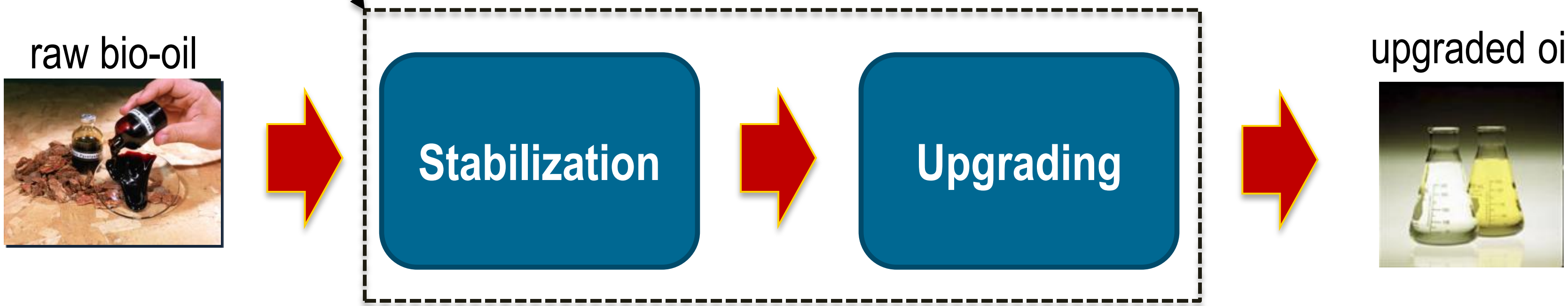
- Tt-E. Liquefaction of biomass and bio-oil Stabilization
- Tt-G. Fuel synthesis and upgrading

Partners

- Oak Ridge National Laboratory
  – Catalyst design, evaluation, scale-up
- Pacific Northwest National Laboratory
  – Reactor evaluation under relevant conditions
- BES User Facilities at ORNL
  – Center for Nanophase Materials Sciences
  – Shared Research Equipment User Facility
  – Micro-scale catalyst characterization
- Univ. of Kentucky
  – Informal collaboration on reactivity study

Project Overview

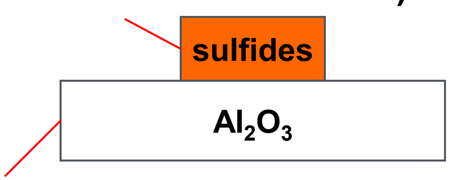
Project focus: hydroprocessing of bio-oils to decrease acid number and oxygen content while maintaining high liquid yields



- Addressing technical barriers identified in BETO MYPP
  - Need for new catalysts with long steady-state operability and high product yields
- Existing catalysts (developed for petroleum) not suitable for bio-oil processes
  - Bio-oils very different from petroleum (low sulfur, high water, high oxygen)

transition-metal sulfides

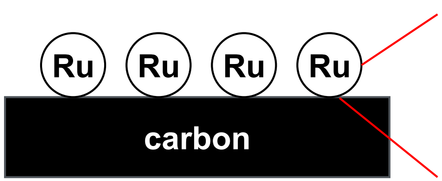
unstable (low sulfur content in bio-oils)



hydrothermally unstable (high water content)

precious metals

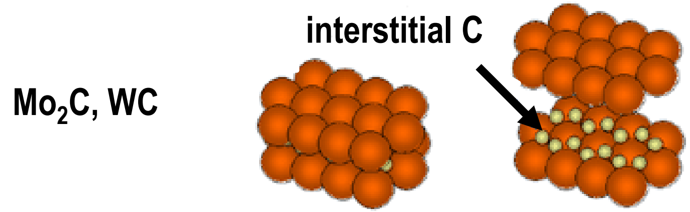
expensive



weak metal-support interaction under reducing conditions

We are developing novel bio-oil hydrotreating catalysts based on transition-metal carbides

- Transition metal carbides exhibit precious-metal-like catalytic properties (Mo_2C vs Ru, WC vs Pt…)



Theory: C insertion to parent metal lattices makes metal electronic structures closer to those of precious metals

- Carbides can be prepared with high surface area
  - No need for supports to disperse catalytically active phases (simpler design compared to Ru/C, $CoMo/Al_2O_3$)
- Carbides are refractory materials
- Recent preliminary study demonstrated the potential of carbides in bio-oil conversion
  - Catalytic reactivity
  - Hydrothermal stability

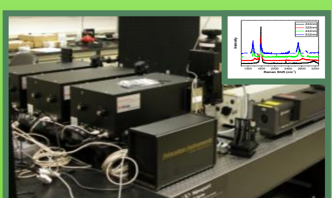
1 - Approach

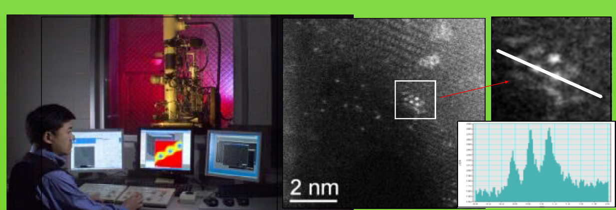
Micro-scale synthesis, characterization, detailed reactivity study

- Understand correlations between carbide synthesis conditions, structures & performance
- Leverage BES & university capabilities

Center for Nanophase Materials Sciences

UK University of Kentucky

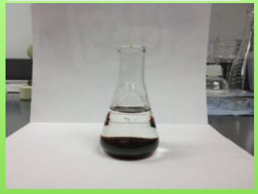




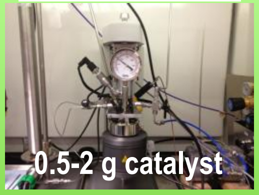
Tailor catalyst performance

Catalyst design, evaluation, scale-up

Model bio-oils



Lab reactors



Reactor evaluation under relevant conditions

Pacific Northwest National Laboratory
Proudly Operated by Battelle Since 1965

- Activity
- Selectivity
- Stability
- Regenerability

Real bio-oils

Pilot flow reactor

Contributors & Collaborators

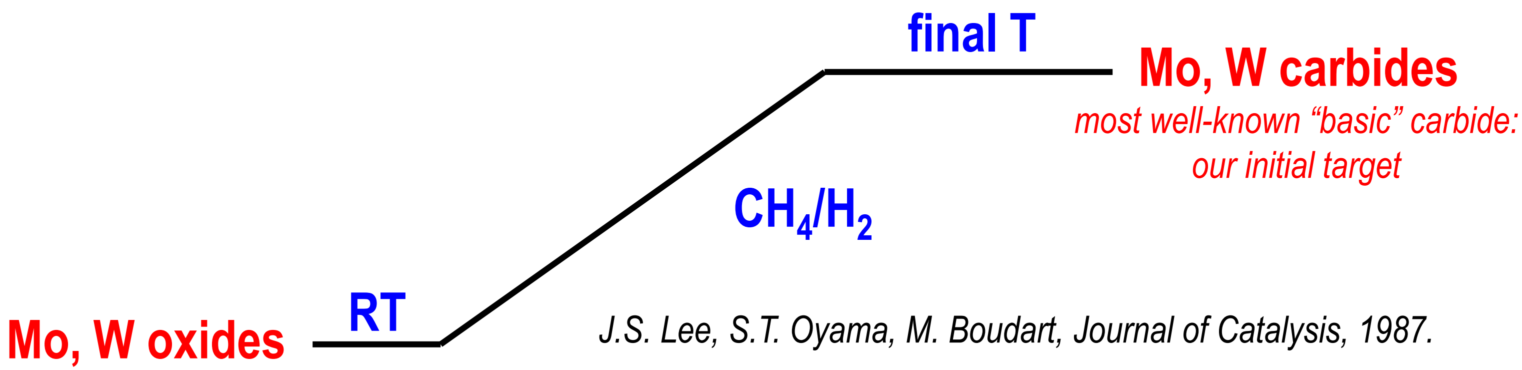
- Viviane Schwartz, Samuel Lewis, Maggie Connatser, Karren More, Harry Meyer, Beth Armstrong, John Henry, Michael Lance, Shirley Waters, Mi-Young Kim, Josh Pihl (ORNL)
  - Oxide precursor shaping, carbide synthesis, characterization, reactor study, analytical chemistry
- Mark Crocker, Eduardo Santillan-Jimenez (Univ. of Kentucky)
  - Aqueous-phase hydrotreating of acetic acid
- Doug Elliott, Todd Hart (PNNL)
  - Reactor study
- DOE BES Research Facilities (ORNL)
  - Center for Nanophase Materials Sciences
  - Shared Research Equipment User Facility
- Seed Money Fund (ORNL)
  - Initial feasibility study

2 - Technical Accomplishments

- Synthesized and characterized a range of bulk Mo and W carbides
- Evaluated hydrothermal stability of candidate catalytic materials
- Began batch-reactor evaluation of carbides using model bio-oils
- Down-selected two Mo carbide formulations with promising hydrotreating performance and stability for pilot-reactor testing
- Developed a method to shape metal-oxide precursors into beads
- Began large-scale carbide synthesis
- Initiating continuous pilot reactor testing

Synthesized and characterized a range of bulk Mo and W carbides

- Carbides prepared by temperature-programmed carburization



J.S. Lee, S.T. Oyama, M. Boudart, Journal of Catalysis, 1987.

  – Control parameters: oxide type, ramping rate, final temperature, gas composition, flow rate, post-treatment etc.

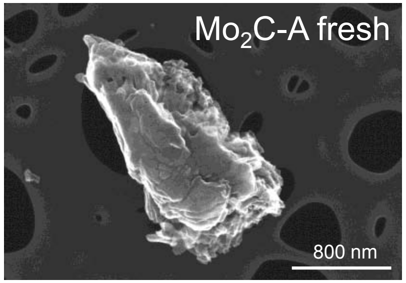
- Characterization performed to obtain information necessary to fine-tune and tailor carbide properties
  – Catalytically relevant structures (e.g., surface area, density of active sites) sensitive to synthesis conditions

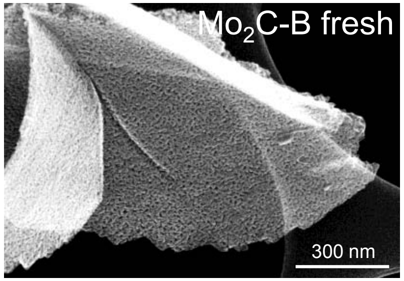
J.S. Choi, G. Bugli, G. Djega-Mariadassou, Journal of Catalysis, 2000.

Structures of carbides can be tuned

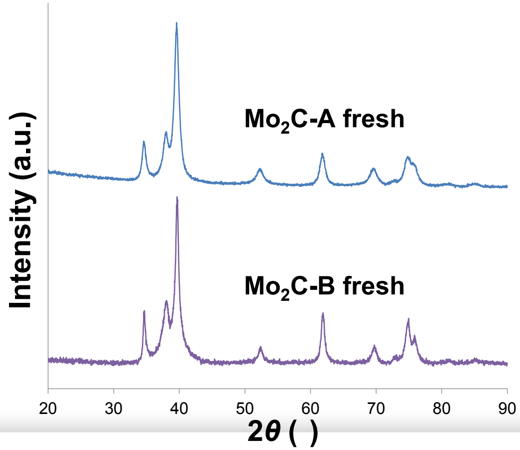
- **Synthesis parameters studied**
  1. Nature of oxide precursor
  2. Final temperature of carburization
- **Impact on carbide structures**
  1. Crystallography
     hexagonal close packed
  2. Surface area
     generally the higher the more active
  3. Density of active sites titrated by CO
     generally the higher the more active

Two Mo_2C samples shown as an example

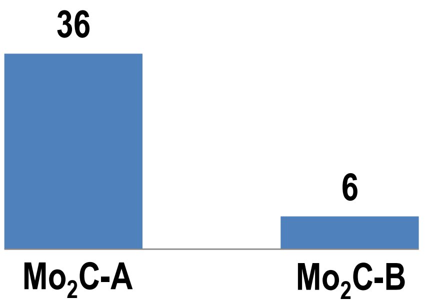




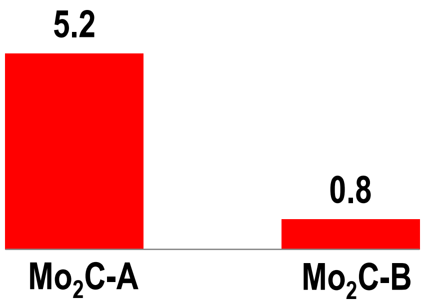
XRD pattern (crystallography)



Surface area (m^2/g_{cat})

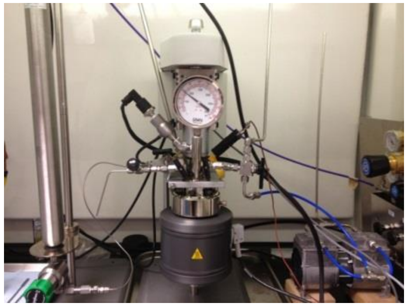


Site density (μmol/m^2)



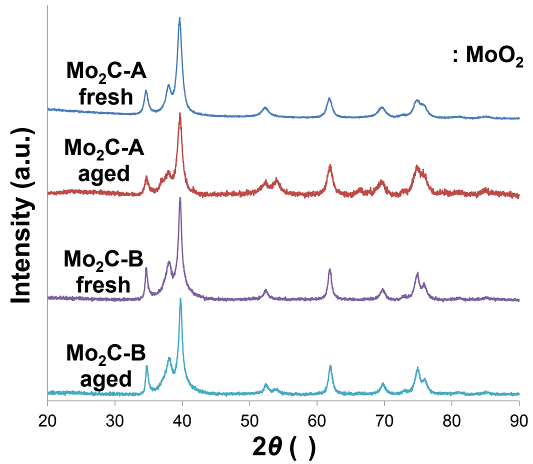
Evaluated hydrothermal stability of candidate materials

- Materials aged in a stirred batch reactor
  - Liquid medium: distilled water
  - Temperature: 250 C
  - Aging duration: 48 h



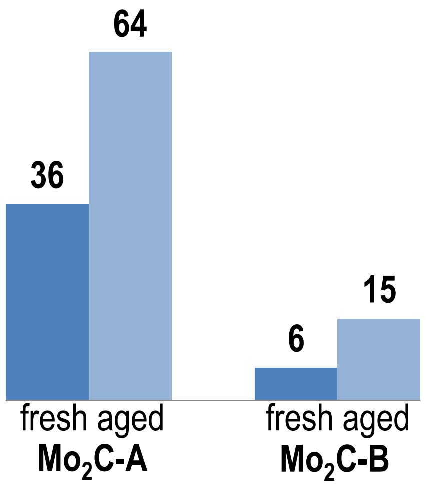
- Characterization performed to study structural changes

XRD pattern



- Mo_2C bulk structure maintained
- Some oxide formation (-)

Surface area (m^2/g_{cat})



- Surface area increased (+)

- Structural evolution sensitive to carbide structures & aging conditions: *can be controlled*

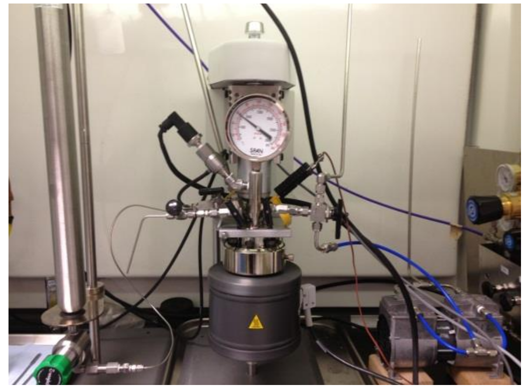
Began batch-reactor evaluation of carbides using model bio-oils

Model bio-oils

- Type 1: 10% acetic acid in water
- Type 2: 5% acetic acid + 5% furfural
  + 5% guaiacol in water

Ref. PNNL model compound study:
D.C. Elliott, T.R. Hart, Energy & Fuels, 2009.

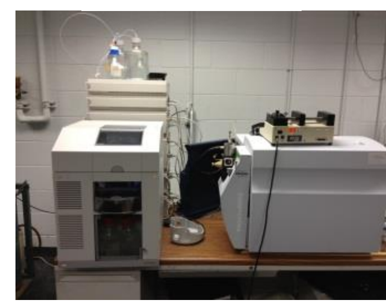
Batch reactor hydrotreating



- Catalyst loading: 0.25-2 g
- Total pressure: 1700-2000 psi
- Temperature: 200-250 °C
- Reaction time: 2-4 h

Products

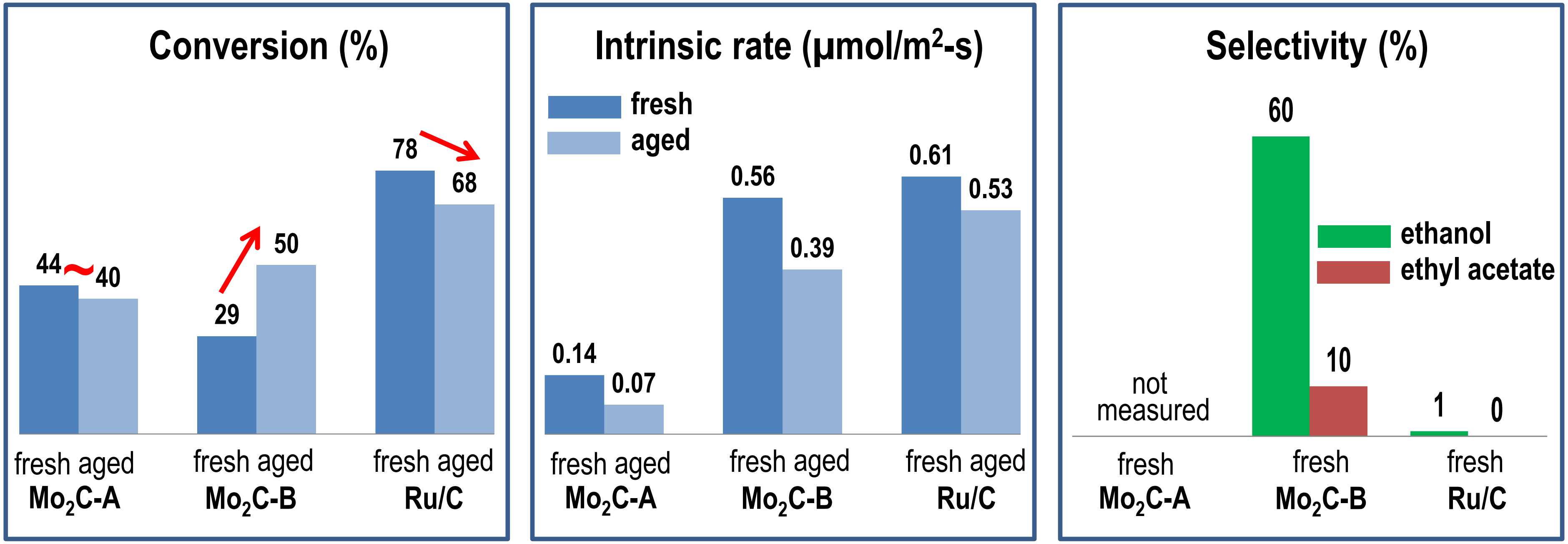
Analysis



- **Model bio-oil study allows quick and reasonable estimation of catalyst performance in real bio-oil upgrading**

Intrinsic activity of Mo_2C in hydrotreating acetic acid comparable to that of Ru/C before and after hydrothermal aging

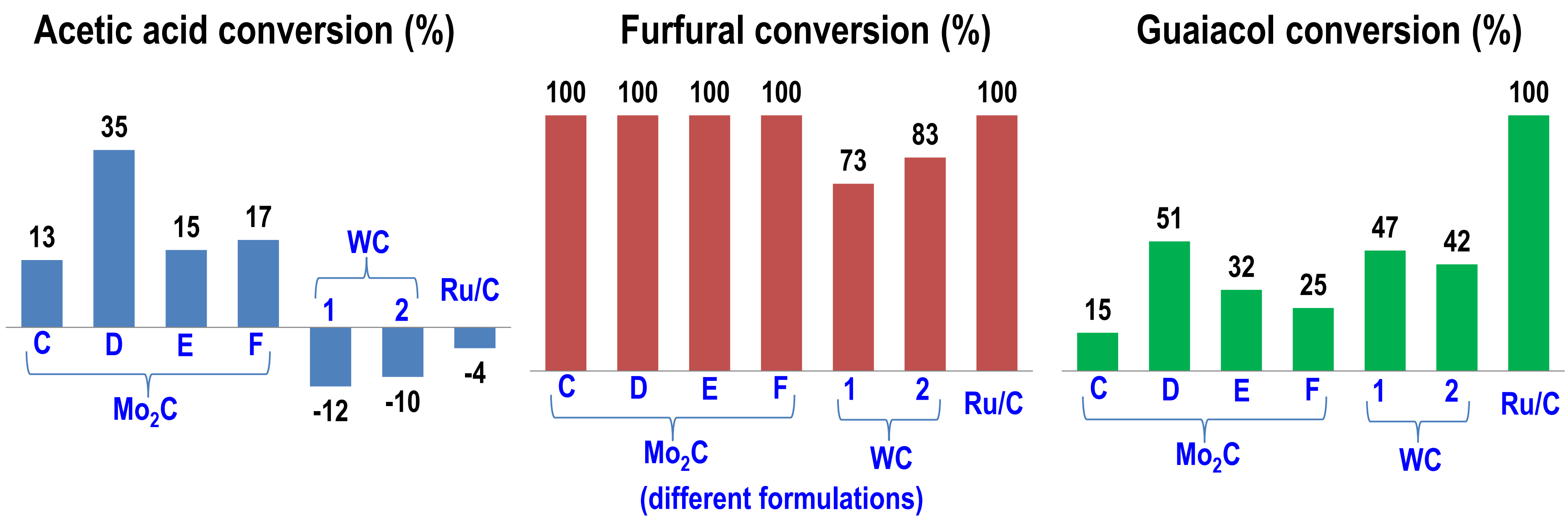
Model bio-oil run type 1: 10% acetic acid in water, 250 °C, 4 h



- Mo_2C active in acetic acid hydrotreating
- Increased surface area of Mo_2C compensated for degraded intrinsic rates with aging
- Mo_2C appears to have higher selectivity for liquid products than Ru/C

Mo_2C showed good performance in converting acetic acid, furfural & guaiacol

Model bio-oil run type 2: 5% acetic acid + 5% furfural + 5% guaiacol in water; 200 °C; 4 h

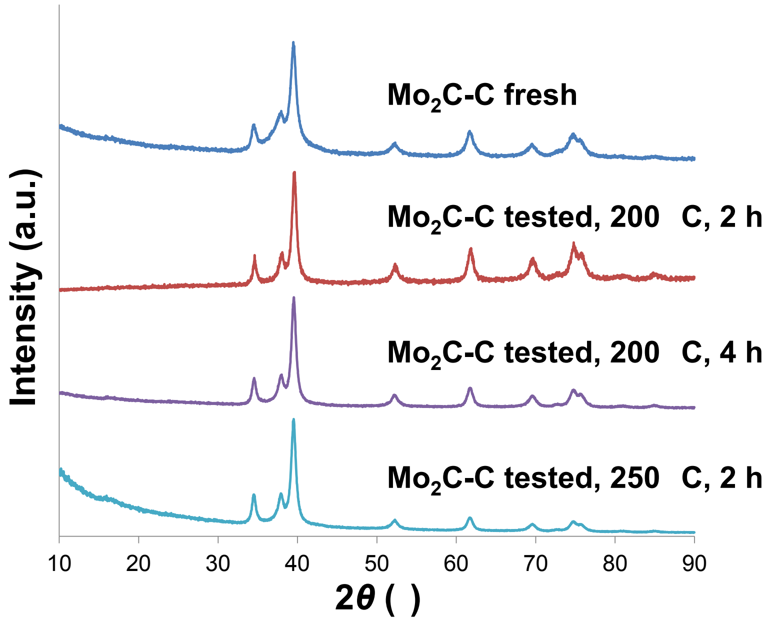


- Mo_2C active in converting all 3 components of model bio-oil
- WC & Ru/C not active in acetic acid conversion (completely inhibited)
  - cf. Ru/C very active in the absence of furfural and guaiacol (previous slide)
- Detailed product analysis in progress (selectivity, mechanisms)

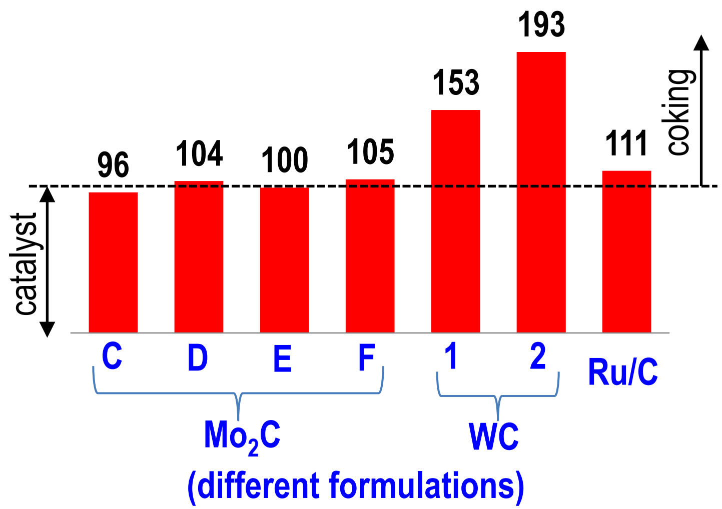
Mo_2C showed good structural stability under reaction conditions with minimal coking

Catalysts analyzed after the model bio-oil run type 2

Unchanged XRD patterns (crystallography)



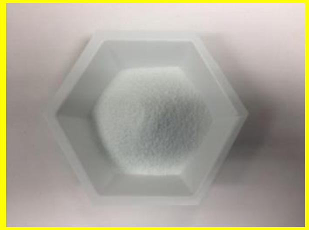
Solid recovery (%)



- Bulk carbide structure maintained without oxide formation
- Mo carbides less prone to coking

Bulk carbide synthesis being scaled up

bulk oxide powder



bulk oxide beads
(9+ formulations)

scale up

Automated bench reactor

bulk Mo_2C beads

- Method developed to shape bulk-metal-oxide precursors
  - Carbides need to be shaped for pilot packed-bed reactor evaluation
  - Shaped bulk metal-oxides not commercially available
- Two down-selected Mo carbides being synthesized (> 200g)
- Synthesis parameters under further optimization

Continuous pilot reactor testing being initiated

Goal: Evaluate performance of select catalysts under relevant conditions

Mo_2C (2 types)

Selected based on batch reactor study with model bio-oils

Real bio-oils

2-stage hydroprocessing

- Perform fixed bed continuous flow upgrading screening tests with real bio-oil
- Regenerate catalysts and examine performance of best regenerable catalysts
- Fuel yield and product quality (by simdis, GC/MS, etc) compared to baseline SOT hydrotreating performance for both first run and regenerated catalysts

Key Milestones/Metrics

ORNL

Title/Performance Measure	Planned Completion Date	Status
Synthesis & characterization of Mo & W carbides with controlled structures (12 formulations)	3/31/2013	√
Initial evaluation of upgrading performance (12 formulations, model & real bio-oils)	06/30/2013	
In-depth kinetic study (4 down-selected formulations, model bio-oil)	09/30/2013	
Stability assessment over 100 h (4 down-selected formulations, model bio-oil)	09/30/2013	

PNNL

Title/Performance Measure	Planned Completion Date	Status
Continuous bio-oil upgrading testing (2 formulations, real bio-oil)	05/30/2013	
Used and regenerated hydrotreating activity testing (2 processed catalysts, real bio-oil)	09/30/2013	

3 - Relevance

- Project aligned with BETO MYPP directly supporting Bio-Oil Pathways strategic goal
  - Develop commercially viable technologies for converting biomass feedstocks into energy dense, fungible liquid fuels, bioproducts and chemical intermediates, and bioenergy

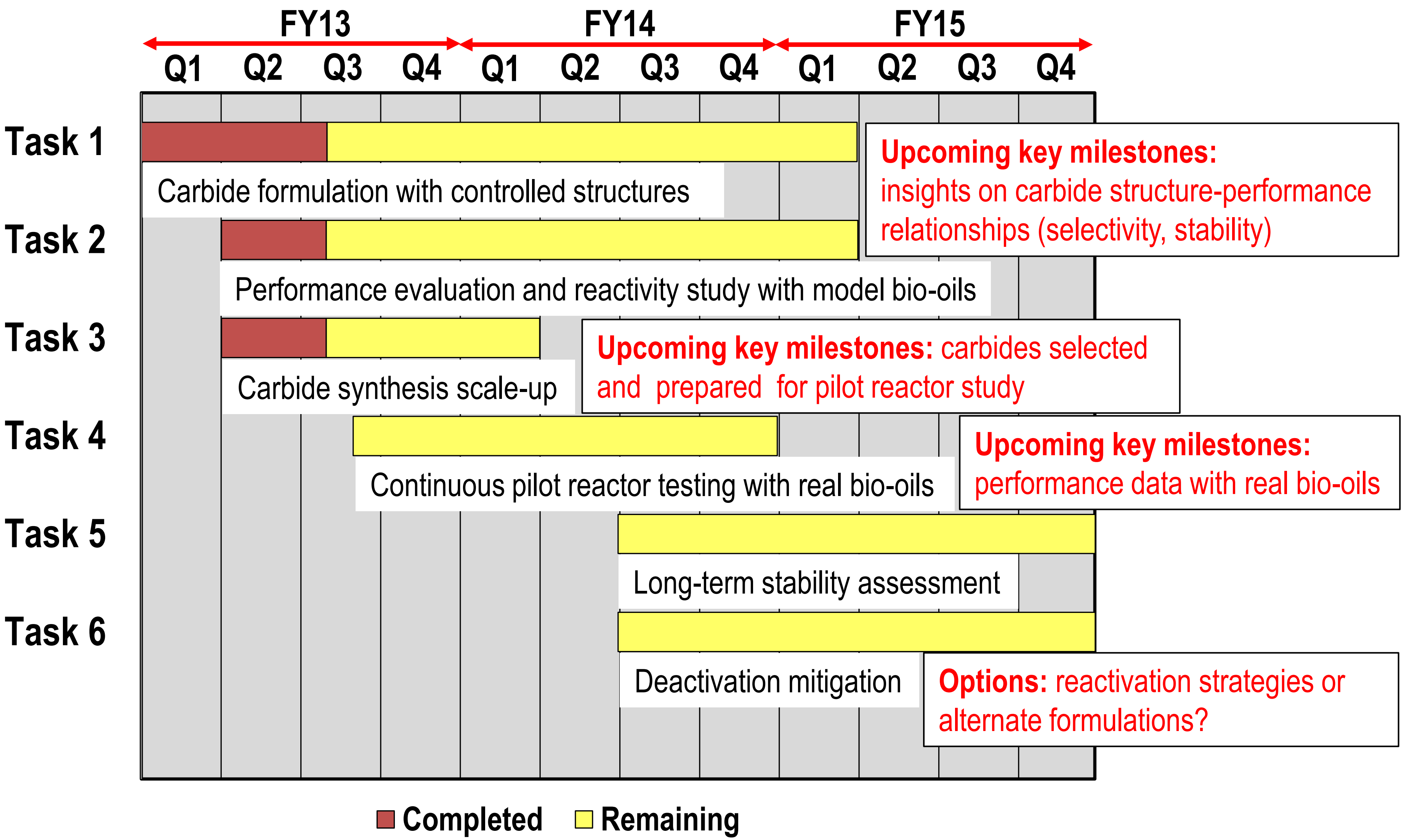
- Research addresses critical technical barriers
  - Tt-E. Liquefaction of biomass and bio-oil stabilization
  - Tt-G. Fuel synthesis and upgrading

- Combined fundamental and applied research provides data required to fully assess the commercial potential of novel catalytic materials for bio-oil hydroprocessing

4 – Critical Success Factors

- Critical success factors
  - Demonstration of large-scale, long-term operation in integrated bio-oil upgrading processes
  - Identification of catalyst structural properties controlling long-term stability
- Challenges to be overcome
  - Limited information and industry experience available in applying carbide catalysts to bio-oil hydroprocesssing
  - Need to scale up the synthesis of bulk carbides for pilot-reactor evaluation
  - Understand and control the impact and interplay among multiple parameters to fully assess the catalysts' potential
- Project impact
  - Developing the next generation of catalysts for conversion of biomass and conditioning of bio-oils is critical in the advancement of biomass processing technologies

5. Future Work



Summary

- **Relevance**
  - Project addresses critical technical barriers, identified in BETO MYPP, to the development of Bio-oil Pathways: need for low-cost, durable and selective catalysts for bio-oil upgrading
- **Approach**
  - Develop novel catalytic materials tailored to the requirements of bio-oil hydroprocessing
  - Fundamental understanding of catalyst structure-reactivity relationships is combined with continuous pilot reactor testing under relevant conditions to guide the development efforts
- **Technical Accomplishments**
  - A range of bulk Mo and W carbides were synthesized, characterized, and evaluated with model bio-oils and two best performing formulations selected for further structure-reactivity study
  - Initial data showed promising performance of bulk Mo carbides in model bio-oil upgrading with respect to activity, selectivity and coking resistance
  - A method of large-scale carbide synthesis has been developed
- **Future Work**
  - Continuous pilot reactor testing with real and model bio-oils for detailed performance data
  - Investigate long-term stability, deactivation mechanisms and mitigation strategies
- **Success factors and challenges**
  - Demonstration of large-scale, long-term operation of integrated bio-oil processes
  - Limited industry experience available in applying carbide catalysts to bio-oil hydroprocessing
- **Technology transfer**
  - Results will be broadly disseminated via collaborations, publications, and invention disclosures.

Additional Slides

Responses to Previous Reviewers' Comments

- Not applicable (new project started in FY2013)

Publications and Presentations

- Jae-Soon Choi, Viviane Schwartz, Eduardo Santillan-Jimenez, Mark Crocker, Samuel A. Lewis, Sr., Harry M. Meyer, III, Karren L. More, "Catalytic performance of molybdenum carbides in aqueous-phase hydrotreating of acetic acid", Preprints of Papers-American Chemical Society, Division of Energy and Fuels Preprints 58 (2013) 1103-1104.
- Jae-Soon Choi, Viviane Schwartz, Eduardo Santillan-Jimenez, Mark Crocker, Samuel A. Lewis, Sr., Harry M. Meyer, III, Karren L. More, "Catalytic performance of molybdenum carbides in aqueous-phase hydrotreating of acetic acid", invited presentation at the 245th ACS National Meeting & Exposition, New Orleans, Louisiana, April 7-11, 2013.
- Jae-Soon Choi, Viviane Schwartz, Eduardo Santillan-Jimenez, Mark Crocker, Samuel A. Lewis, Sr., Harry M. Meyer, III, Karren L. More, "Catalytic Activity and Stability of Molybdenum Carbides in Aqueous Phase Hydrotreating of Acetic Acid", to be presented (oral) at the 23rd North American Catalysis Society Meeting (NAM), Louisville, KY, June 2-7, 2013.