HyMARC Seedling: A Reversible Liquid Hydrogen Carrier System Based on Ammonium Formate and Captured CO_2

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Project ID #: **ST217**

Overview

Timeline

- Project start date: 1 October 2019
- (Funds received Feb 2020)
- Project end date: Jan. 31, 2023*

*Project continuation and direction determined annually by DOE

Barriers

A. Catalyst cost
B. Energy efficiency
C. Durability

Budget

- Funding received in FY20

-- $ 339,972 (including $53,939 to partner)
-- total cost share is $87,748

Partners

Project Lead: WSU

Interactions/Collaborations

- 8 Rivers

Relevance

Objectives: build a prototype ammonium formate-based hydrogen uptake and release system and evaluate its techno-economic potential for commercialization. During the first year of this project (current reporting your), we have accomplished:

- Collect the baseline performance data with the commercial Pd/C catalyst in the laboratory-scale batch reactors.
- Develop the next-generation hydrogenation/dehydrogenation catalysts that reduce *up to 50 % of the Pd loading* while keeping the comparable catalytic activity compared to the commercial Pd/C catalyst.
- The mechanistic studies are underway through the collaboration the LLNL group in HyMARC.
- Design and build a continuous CSTR (reactor volume is 10X larger than the batch reactors) for process scale up and long-term catalyst durability evaluation.
- Perform initial technoeconomic analysis (TEA) of the Levelized H_2 delivery cost using the ammonium formate carrier at the large-scale (50,000 kg H_2 / day).

Approaches / Milestone

Milestone 1. Collect the baseline performance data at the laboratory scale (FY20 Q1-Q2)

1.1 Demonstrate the laboratory-scale reversible hydrogenation/dehydrogenation processes with the commercial Pd/C catalyst. **100%**

1.2 Approve the baseline performance data for the project. **100%**

Milestone 2. Development, synthesis and evaluation of the next-generation catalysts (FY20 Q3-Q4)

2.1 Synthesize 5 g of a minimum of 5 new catalysts for evaluation. **100%**

2.2 Determine the best-performed catalyst according to the selection criteria. **100%**

Go / No Go #1 (09/30/2021)

Demonstrate the baseline performance and economic data of using the ammonium formate hydrogen carrier to be achieved over the best-performed catalyst in the laboratory-scale 50-ml reactors, including:

- the fast hydrogen uptake/release kinetics under mild operation conditions (turnover frequency, i.e., TOF > 1000 h^{-1} at 20-80°C and 5-50 bar); **100%**
- a good short-term catalyst stability (>10 cycles of hydrogenation / dehydrogenation); **80%**
- a reasonable cost of the Levelized H_2 delivery at the beginning of the project (<1.5x H_2 delivery cost in 700 bar tank trailer) **50%**

Approaches: Development of the next-generation catalysts

Functionalize carbon support

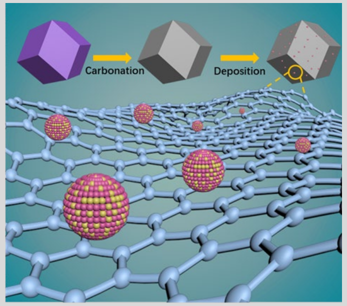
N- doped carbon

O- functionalized carbon

Optimize metal species

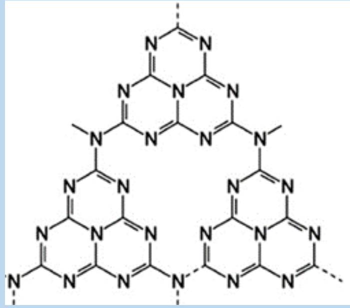
Synergistic effect

MOF template



- ✓ High activity
- ✓ Low Pd loading
- Multiple-steps preparation
- Complex system

g-C_3N_4

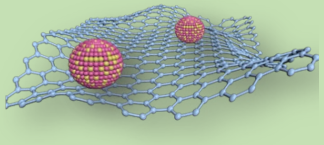


- ✓ Moderate Activity
- Marginal stability

Acid-wash treatment

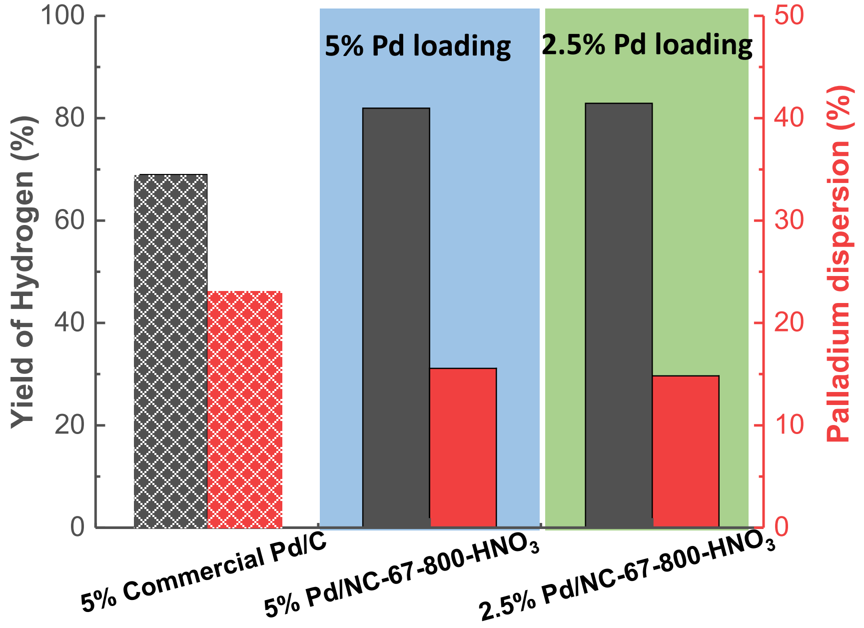
- ✓ Easy to scale-up
- ✓ High Pd dispersion
- ✓ Good stability

Pd-M bimetallic

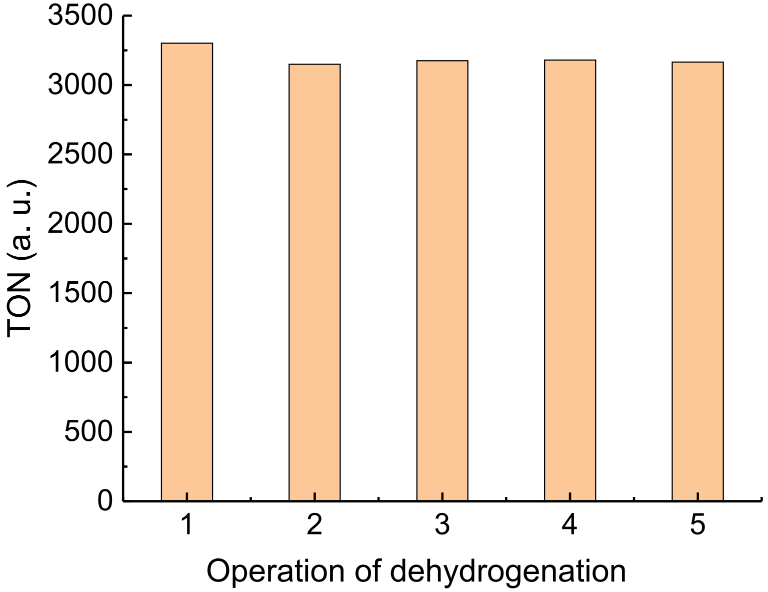


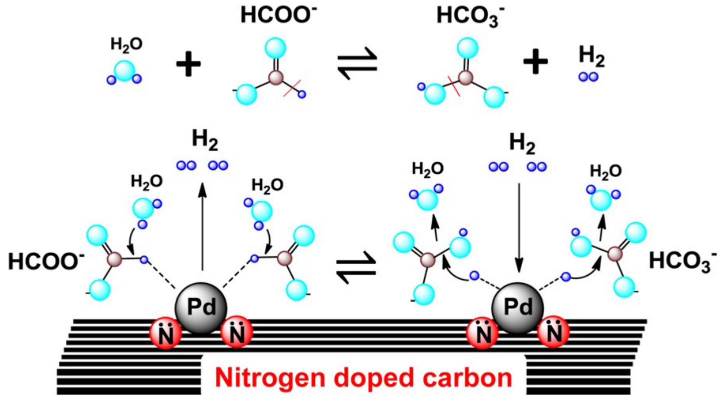
- ✓ High Activity
- ✓ Low cost
- ✓ Low Pd loading
- ✓ Good stability

Accomplishment: Developed MOF-templated synthesis of N-doped carbon support to improve efficiency of Pd catalyst



1 M ammonium formate, 0.09 g catalyst, 80 °C.





ChemSusChem 2016, 9, 246-251.

- **High-efficient Pd utilization.**
  - Reduced the Pd loading by a factor of **50%** while the H_2 yield increased **17%** compared to the commercial Pd/C catalyst .
- **Good stability.**
  - TON was nearly unchanged after 5 repeated dehydrogenation runs.
  - The spent catalyst was regenerated between each run.

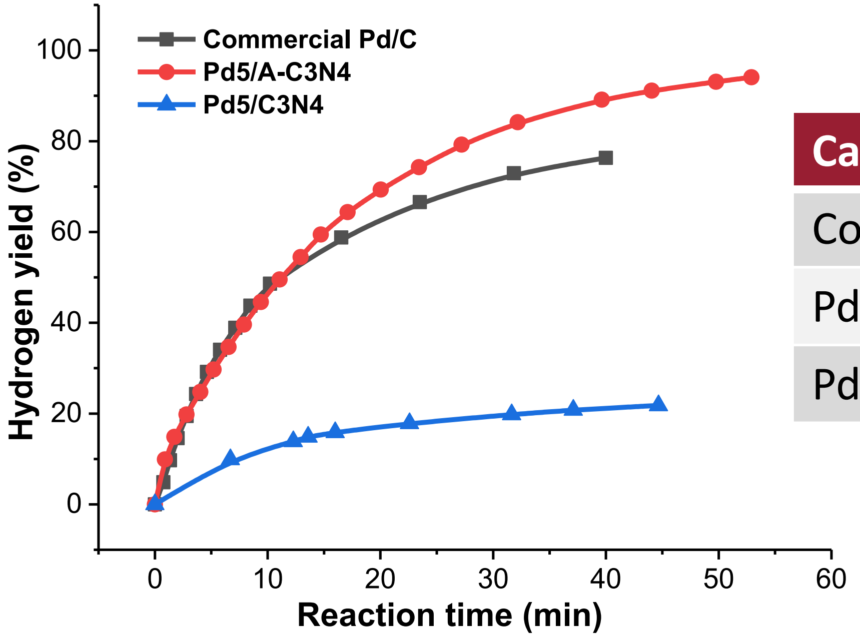
Challenges

- **Multi-step preparation.**
  - ZIF synthesis, carbonation, wash & dry, pre-treatment, wash & dry, precipitation, reduction.
  - Scaling up the synthesis is challenging.
- **Complex mechanism.**
  - Residual non-noble metal species, oxygen-containing functional groups, N-doped species, etc.

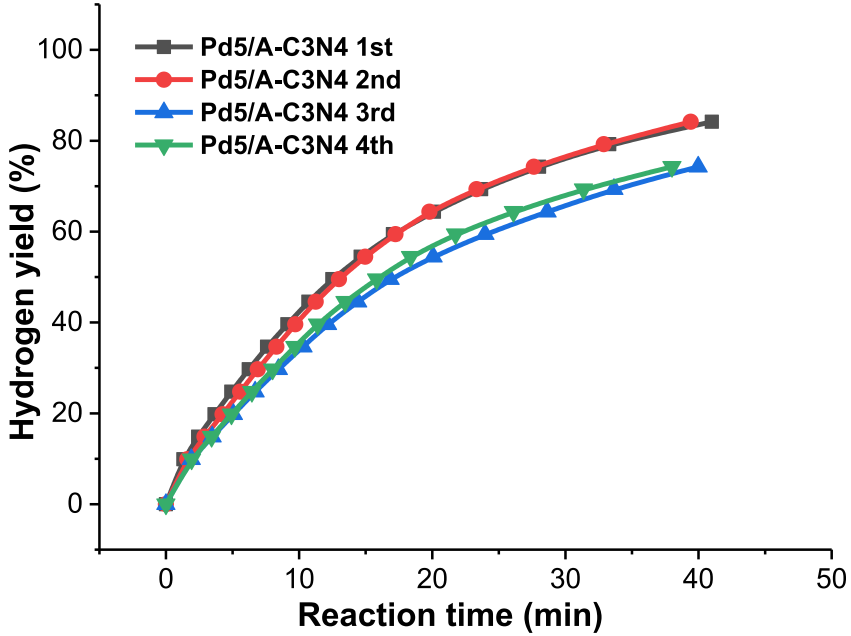
Mechanism

- Nitrogen species on the carbon support may positively polarize the carbon in the bicarbonate or formate molecules, facilitating their absorption on the catalyst through electrostatic interaction.

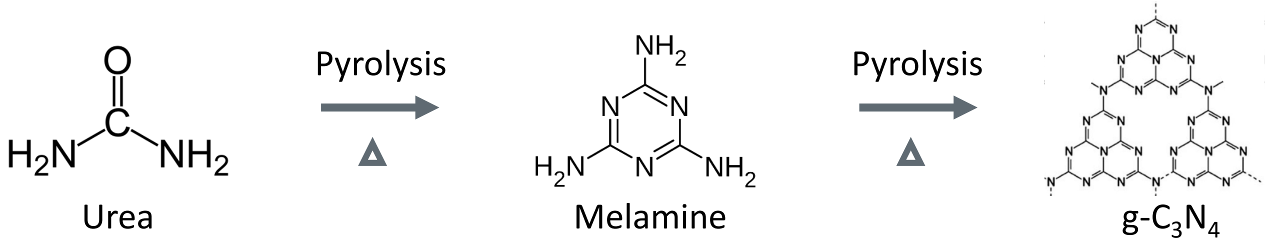
Accomplishment: Developed a facile synthesis of C3N4 support to improve efficiency of Pd catalyst



Catalyst	H2 yield
Commercial Pd/C	78.7%
Pd5/C3N4	21.8%
Pd5/A-C3N4	89.1%



Run	1st	2nd	3rd	4th
H_2 yield	84.2%	84.2%	74.3%	74.3%



- A facile C3N4 synthesis procedure was developed.
- The as-synthesized Pd/C3N4 catalyst can be activated through an acid-wash treatment.
- The stability of the Pd/C3N4 catalyst is unsatisfied.

Accomplishment: Developed a facile synthesis of O-functionalized carbon-supported Pd catalyst to improve efficiency


Acid-wash treatment

impregnation

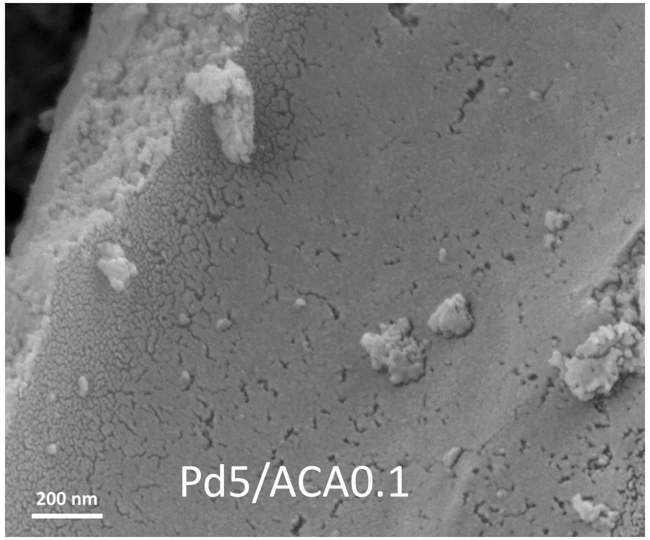
$NaBH_4$

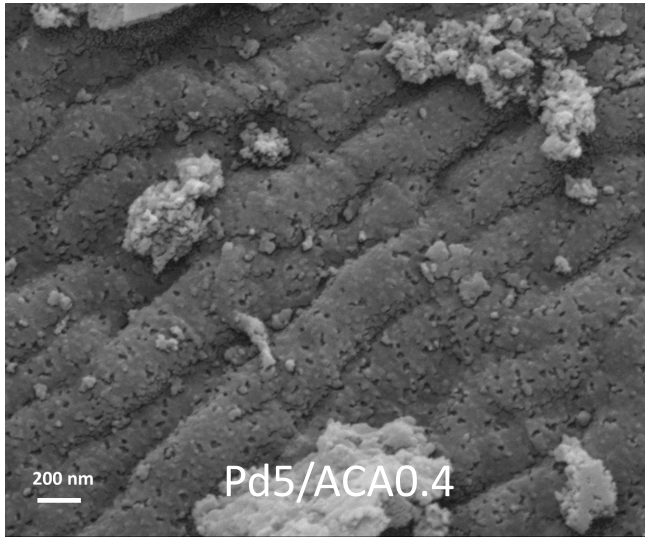
Commercial carbon support

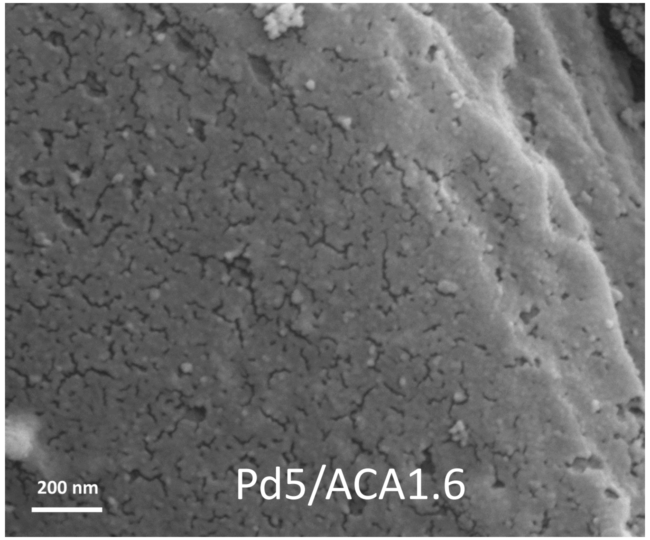
Pd/ACAx catalysts

Acid-wash treatment

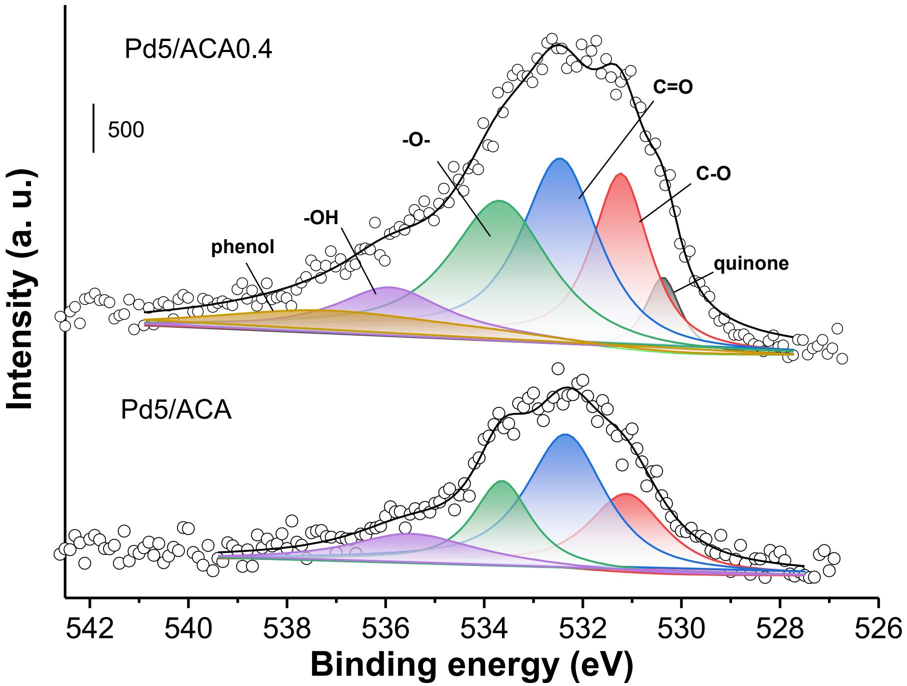
- Create more defects or disordered sites on the carbon support by the acid-wash treatment.
- Introduce more surface oxygen-containing functional groups (carbonyl, hydroxyl, etc.) on the carbon support.
- High Pd dispersion was realized on the carbon support treated with concentrated acid.



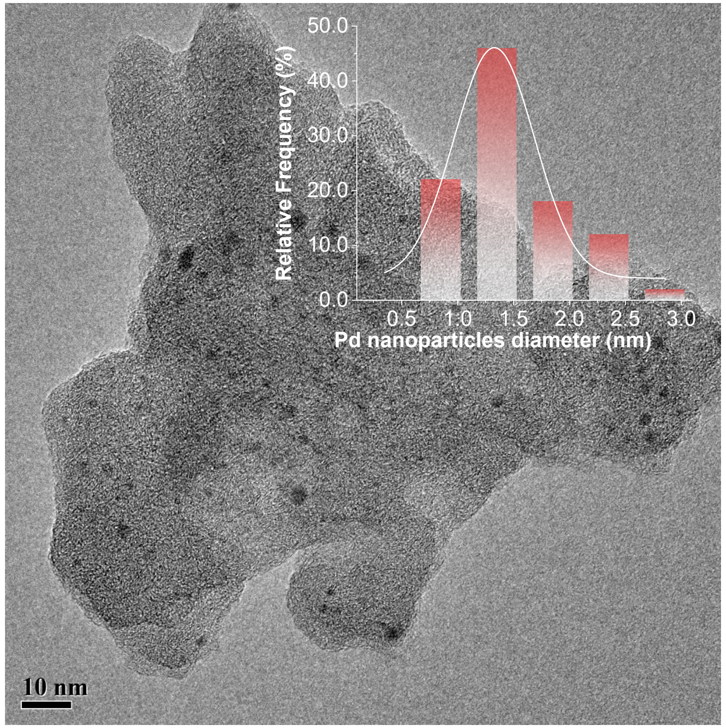




Accomplishment: Elucidate structure-activity relationship of Pd/ACA catalysts via characterization



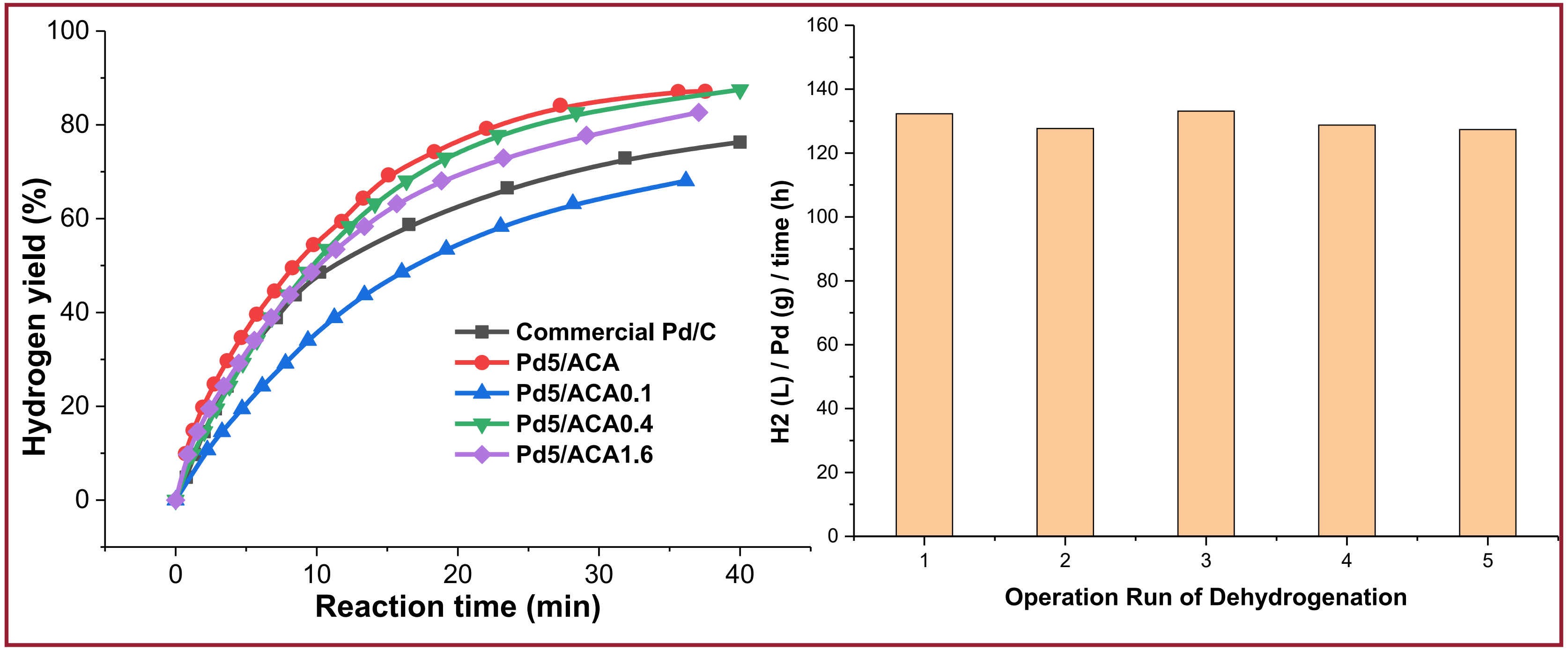
O-species content (atom%)	Pd5/ACA0.4	Pd5/ACA
quinone	0.499	-
C=O (ketone)	1.913	1.178
-COOH (carboxylic)	2.685	2.066
-O- (ether)	2.514	0.919
-OH (hydroxyl)	0.811	0.608
phenol	0.707	-
Total	**9.13**	**4.77**

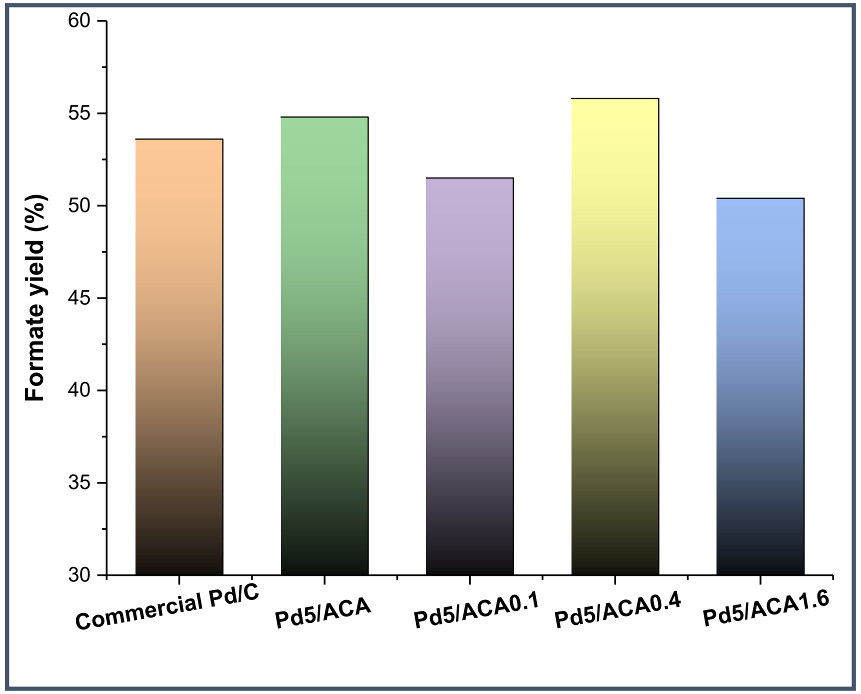


TEM image of Pd/ACA0.4

Catalyst	Pd dispersion (%)
Commercial Pd/C	23.0
Pd5/ACA	37.0
Pd5/ACA0.1	37.1
Pd5/ACA0.4	42.9
Pd5/ACA1.6	44.7

Accomplishment: Down-selection of the best performed Pd/ACA catalysts via kinetic study





The acid-wash treatment of the carbon support enhanced the activity of the Pd/ACA catalysts compared with commercial Pd/C

Dehydrogenation:

- Final H_2 yield (88.5% vs. 78.7%, **12.5%** improvement);

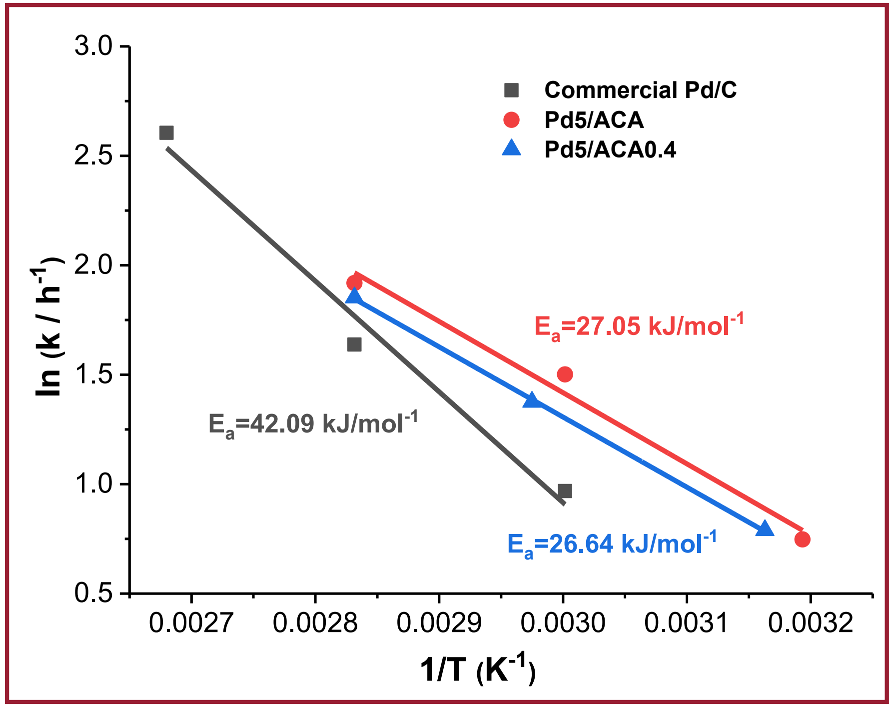
Hydrogenation:

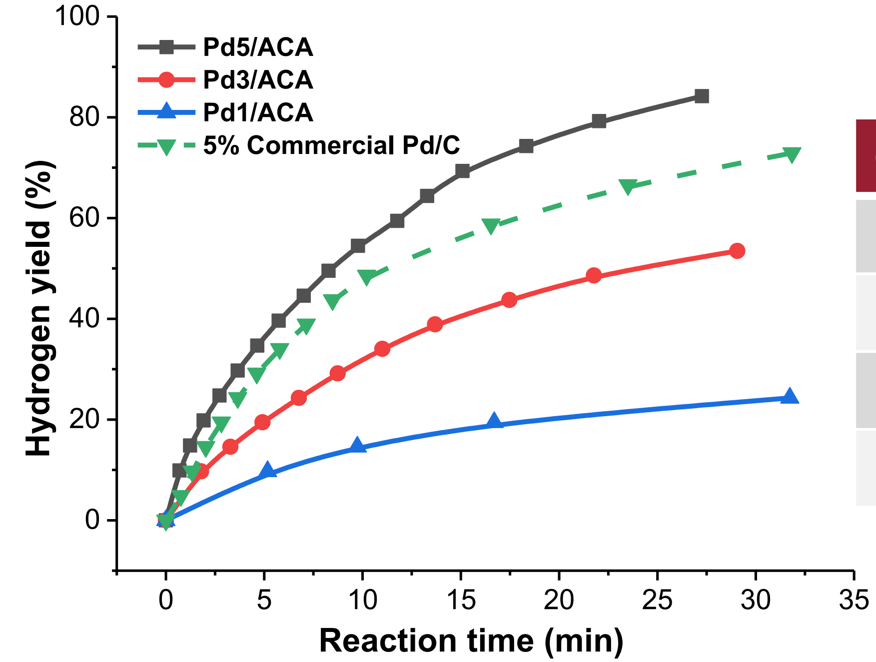
- Formate yield for a 2-h reaction (55.8% vs. 53.6%, **4.1%** improvement);

Stability:

- Pd5/ACA0.4 was stable for 5 runs of the dehydrogenation reaction.

Accomplishment: Elucidate structure-activity relationship of Pd/ACA catalysts via kinetic study





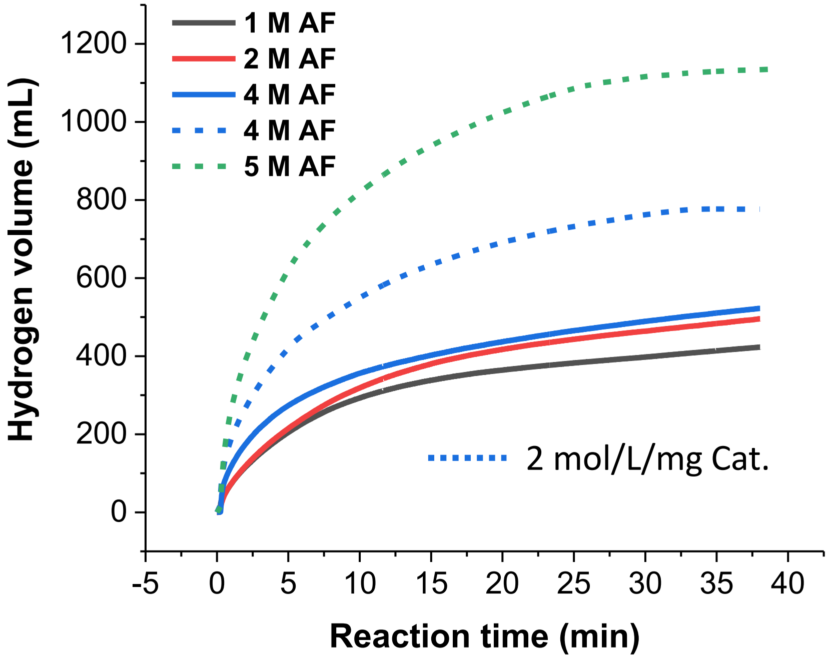
Catalyst	H_2 yield
Commercial Pd/C	72.9%
Pd5/ACA	84.1%
Pd3/ACA	53.5%
Pd1/ACA	24.3%

Advantages: **High Pd dispersion; High H_2 yield; Low activation energy.**

- Pd dispersion (44.7% vs. 23%, **94.3%** improvement)
- Activation energy (26.6 vs. 42.1 kJ/mol, **36.7%** decrease)

Challenges: **High Pd loading is still needed to deliver a high H_2 yield. The investigation of the catalytic reaction mechanism is underway.**

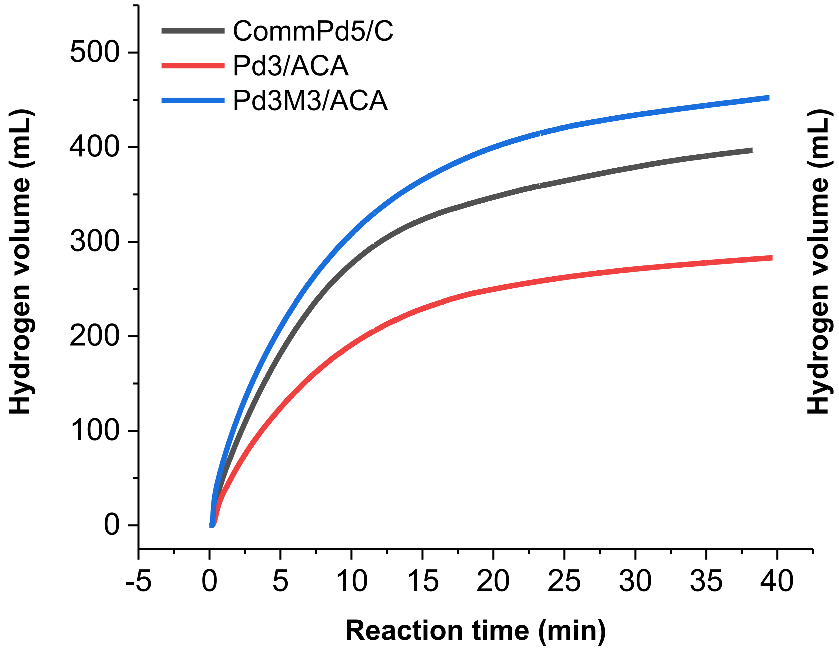
Accomplishment: Demonstration of high H_2 releasing rate from concentrated ammonium formate

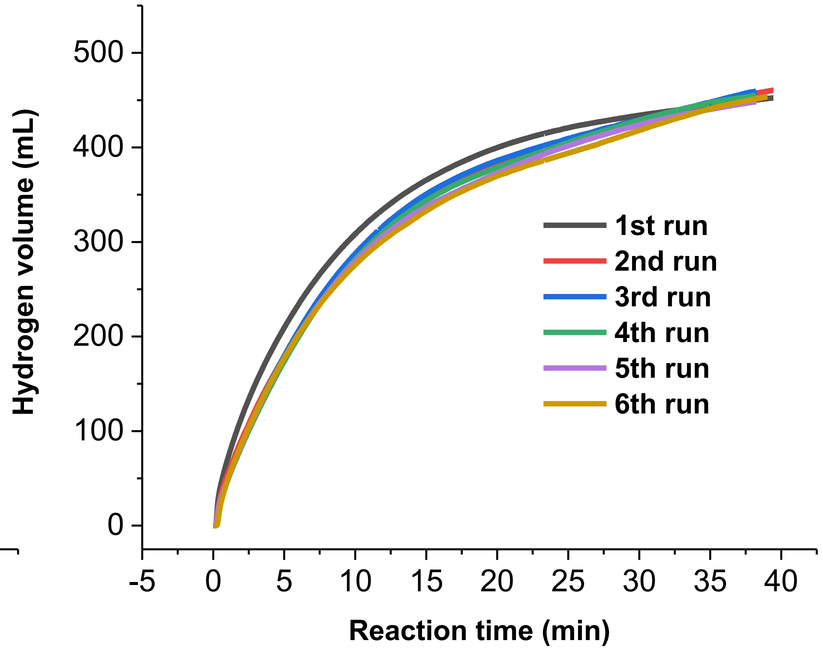


Ammonium Formate Concentration	Catalyst usage	H_2 yield in mL/hr
1M	0.1 g	635
2M	0.1 g	744
4M	0.1 g	783
4M (dash)	0.2 g	1166
5M (dash)	0.25 g	1701

- High ammonium formate (AF) concentration substantially increases the H_2 yield.
- Higher catalyst loading is required to obtain high H_2 yield from concentrated AF.
- The optimization of the formate concentration and the catalyst loading is underway.

Accomplishment: Development of a facile synthesis of Pd-M bimetallic catalysts for enhanced performance





Activity		**Pd3M3/ACA Stability**	
Catalyst	V_{H2} in 40 mins	Run	V_{H2} in 40 mins
CommPd/C	397mL	1st	452mL
Pd3/ACA	283mL	2nd	460mL
Pd3M3/ACA	**452mL**	3rd	459mL
		4th	455mL
		5th	448mL
		6th	453mL

Bimetallic Pd-M/ACA catalyst (The second metal is 100X cheaper than Pd) shows much improved dehydrogenation performance compared with the commercial Pd/C catalyst

- High initial dehydrogenation rate (41.9 mL/min vs. 36.4 mL/min, **15%** improvement);
- High H_2 yield (89.3% vs. 78.7%, **13.5%** improvement with a **40.0% less Pd loading**);
- Short-term catalyst stability is demonstrated for consecutive 6 runs of dehydrogenation.
- Mechanistic studies are underway.

Accomplishment: summary of TOF of the selected best performed next-generation catalysts

Entry	Catalysts	H_2 (L)/Pd (g)/time (h)	TOF (h^{-1})
1	Commercial Pd/C	114.9	5246.0
2	Pd5/NC	137.8	13103.8
3	Pd2.5/NC	273.2	17078.7
4	Pd5/ACA	137.6	3985.7
5	Pd5/ACA0.1	105.1	2601.8
6	Pd5/ACA0.4	132.3	3190.7
7	Pd5/ACA1.6	99.9	3059.2
8	Pd3M3/ACA	229.1	11634.5#

- TOF, (mole of H_2)/(mole of Pd *dispersion ratio of Pd *time), is calculated with the average initial reaction rates in the first 10 mins of the reaction in the batch reactor.
- # Assume that Pd was the active site for dehydrogenation.

The best performed next-generation catalysts have a 2X higher TOF than the commercial Pd/C catalyst or >10X higher TOF than the GN1 target.

Accomplishment: TEA is underway*

Levelized Cost of H_2 Delivery

- Comparison data were taken from ANL H_2 carrier webinar presentation (Apr. 2019)
- Assumptions:
  - Capacity factor: 90%
  - Fuel: $6/MMBtu
  - Electricity $57.4/MWh
  - Water 0.54 C/gal
  - Ammonium bicarbonate: $100/tonne (2.5% makeup)

Levelized Cost of H_2 distributed to Stations (50 tpd-H_2) ($/kg)

	GH2	Methanol	Ammonia	MCH	AF
Small scenario	4.95	6.61	7.42	6.45	TBD
Large scenario		4.98	6.48	6.65	TBD

- Ammonium formate (AF)-based system is thermodynamically more favorable than other LOHCs such as methyl cyclohexane (MCH)
- The catalyst performance is the key to lower the capital cost of the AF-based LOHC system.
- The water dilution increases the volume of AF carrier to be transported, negating some energy efficiency advantages.
- To be competitive with MCH, it is recommended that the volume of AF products must be reduced which can be done in two ways:
  - ✓ Reducing the water content of final AF solution prior to transportation by integrating with low-grade heat available in the power plant
  - ✓ Operating in the highly-concentrated bicarbonate/formate regime and catalyst performance in highly-concentrated environment should be investigated to ensure high stability and activity

** Due to the impact of COVID, the research on TEA is delayed.*

Response to previous year's review

This project was not reviewed last years

Collaboration and Coordination

Core Project Team monthly videoconference meetings and frequent email communications occur among all WSU and 8Rivers investigators. WSU (Lin) is leading the whole project and is focusing on developing the next-generation catalyst in **BP1**). 8 Rivers Capital LLC (Rafati, Cross) are leading the technoeconomic analysis and the scale-up process design and integration

HyMARC Collaboration monthly videoconference meetings occur between the WSU group (Lin) and our HyMARC contact at PNNL (Grubel, Brooks, Autry). This enables the seed project team plan for technology validation and transfer. WSU is also collaborating with other HyMARC team members in this seeding project, including NREL (Leick for TPD/MS characterization), LLNL (Akhade and Wood for DFT simulation), SNL (Stavila for MOF materials) and LBNL (Su for catalyst development)

Remaining Barriers and Challenges

For development of next-generation catalyst

- The catalytic performance of the ACA carbon supported Pd bimetallic catalysts needs to be optimized and the catalytic reaction mechanism will be investigated.
- In-situ characterizations are insufficient to understand the dynamic change of the physicochemical properties of the catalysts. We will purchase a high-pressure and high-temperature ATR cell for in-situ FTIR study.
- The durability and reusability of the next-generation catalysts need to further investigated and long-term stability of the catalysts needs to be demonstrated.

For process design and integration

- 8Rivers is developing multiple technologies that could be integrated with this project, such as CO_2 capture, H_2 production, etc. Leveraging the existing industrial infrastructure could significantly reduce the production cost of the AF-based LOHC.

Proposed future work

Milestone #	Project milestones	Completion date	Percent completed
GN1	Demonstrate the baseline performance and economic data of using the ammonium formate hydrogen carrier to be achieved over the best-performed catalyst in the laboratory-scale 50-ml reactors, including: I. the fast hydrogen uptake/release kinetics under mild operation conditions (turnover frequency, i.e., TOF > 1000 h^{-1} at 20-80°C and 5-50 bar); II. a good short-term catalyst stability (>10 cycles of hydrogenation / dehydrogenation); and III. a reasonable cost of the Levelized H_2 delivery at the beginning of the project (<1.5x H_2 delivery cost in 700 bar tank trailer).	09/30/21	90%
M3.1	Synthesize up to 500 g of the selected best- performed catalyst.	12/30/21	10%
M3.2	Demonstrate the prototype CO_2-to-formate process that will be fully functional to produce formate using pressurized CO_2 and H_2 gases as the feedstock	6/30/22	Not start

- Any proposed future work is subject to change based on funding level

Publications & Presentations

- Z. Dong, A. Mukhtar, H. Lin, Heterogeneous Catalysis on Liquid Organic Hydrogen Carriers. Submitted to Topics in Catalysis (Under review)

Summary

Objectives: Build a prototype ammonium formate-based hydrogen uptake and release system and evaluate its techno-economic potential for commercialization.

Relevance:

- Collect performance data of commercial Pd/C and perform baseline TEA, identifying the key drivers to lower the levelized H_2 delivery cost using the ammonium formate-based liquid organic hydrogen carrier.
- Develop the next-generation hydrogenation/dehydrogenation catalysts and demonstrate that the new catalysts via three different synthesis approaches are superior to the commercial catalyst.

Approaches: Develop next-generation catalysts by functionalizing carbon supports, improving metal size and dispersion, and optimizing bimetallic compositions.

Accomplishment:

- N and O functionalized carbon supported Pd catalysts show enhanced dehydrogenation/hydrogenation performance than commercial Pd/C.
- The Pd-M bimetallic catalysts show superior catalytic performance with a lower Pd loading (40% less than the commercial catalyst).
- The best performed next-generation catalysts have a 2X higher TOF than the commercial Pd/C catalyst or >10X higher TOF than the GN1 target.