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

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DOE Hydrogen Program
2022 Annual Merit Review and Peer Evaluation Meeting

AMR Project ID: ST217

DOE HyMARC Program 2022 Annual Merit Review and Peer Evaluation Meeting

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Project Goals

- Development of highly efficient and cost-effective Pd-based heterogeneous catalysts for fast kinetics of hydrogen uptake and release using ammonium formate / bicarbonate based liquid organic hydrogen carrier system under mild conditions (20-80°C and 1-50 bar).

- Demonstration of excellent short-term stability of the Pd-based heterogeneous catalysts (up to 10-cycles) by maintaining the >90% of initial hydrogen uptake and release activity.

- Development of a techno-economic process model to assess the cost of H_2 delivery with ammonium formate-based hydrogen carriers, to quantify economic uncertainty and risk in the model results, and to guide the research and development.

Overview

Timeline

Project Start Date: 12th February 2020
Project End Date*: 31st January 2024**

**Project date was extended due to COVID-19.*
***Project continuation and direction annually determined by DOE.*

Budget

DOE Funding received in FY21: $0 (no-cost extension)
DOE Funding received to date: $427,720 ($339,972 federal funds and $87,748 cost share by WSU and 8Rivers).

Partners

- Washington State University
- 8 Rivers Capital, LLC.

Collaborators

- Pacific Northwest National Laboratory
- Lawrence Livermore National Laboratory
- National Renewable Energy Laboratory
- Lawrence Berkeley National Laboratory

Relevance

- **Objectives:**

  This project aims to develop a prototype ammonium formate / bicarbonate-based liquid organic hydrogen carrier for hydrogen storage, transportation, and delivery system and perform a preliminary techno-economic analysis for evaluate economic feasibility for commercialization.

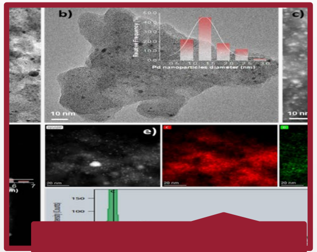
Barriers from DOE Targets	Our Technical Targets
The state-of-the-art hydrogen storage technologies are cost-intensive.	Perform a preliminary techno-economic assessment and sensitivity analysis to identify research targets to improve the overall process economics.
The state-of-the-art liquid organic hydrogen carriers are not energy-efficient.	Demonstrate fast kinetics for H_2 uptake and release with the next-generation catalysts under mild conditions.
Inadequate durability of hydrogen storage systems.	Demonstrate 10-cycle stability (maintaining >90% of original activity) for H_2 uptake and release.

Approach

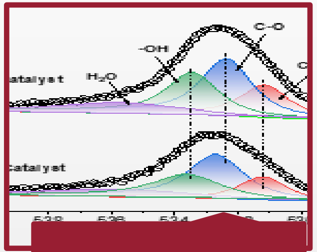
- ## Approach:

Develop the next-generation supported Palladium (Pd) catalysts with varying Pd-metal contents (1-5 wt.%) and perform the catalyst evaluation, stability test, and techno-economic analysis.

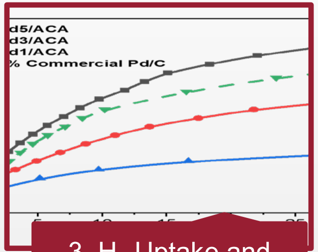
- **Novel catalyst synthesis approaches**:
  - Decorate carbon support surfaces with O-functional groups to enhance the metal-support interactions.
  - Incorporate the second metal into the supported Pd catalyst and precisely tune the metal atomic ratio.
- **Comprehensive catalyst characterizations:**
  - Catalyst surface adsorbates and electronic structure variation were investigated and monitored in-situ by advanced characterization techniques.
- **Techno-economic analysis guided research:**
  - The TEA results identify the sensitive parameters and further provide the guidance of modifying the research targets.



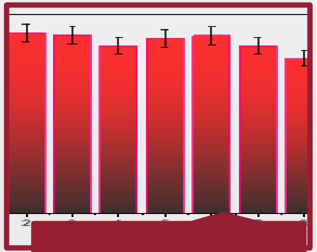
1. Synthesis



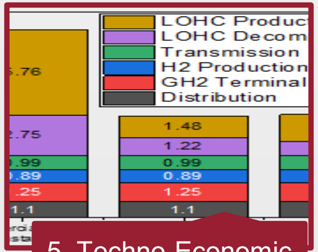
2. Characterization



3. H_2 Uptake and Release Evaluation



4. Stability



5. Techno-Economic Analysis

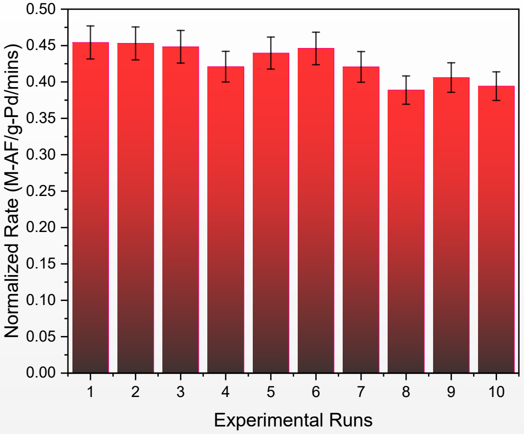
Accomplishments – Demonstrate fast H_2 Uptake/Release kinetics

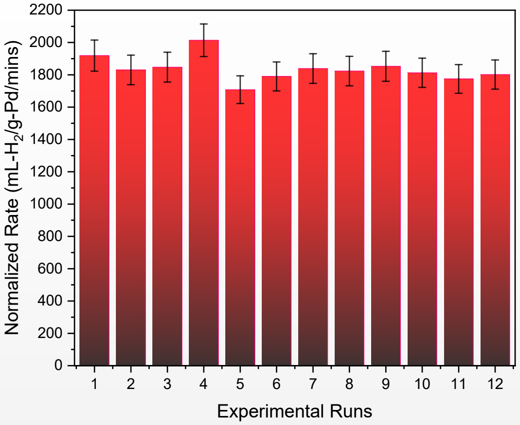
Process	Catalysts	GNG Target TOF (h^{-1})	Achievements TOF (h^{-1})
Hydrogenation	Commercial Pd/C	1000	1480
	Pd/WSU-1 Catalyst		1477
Dehydrogenation	Commercial Pd/C		3106
	Pd/WSU-2 Catalyst		14275

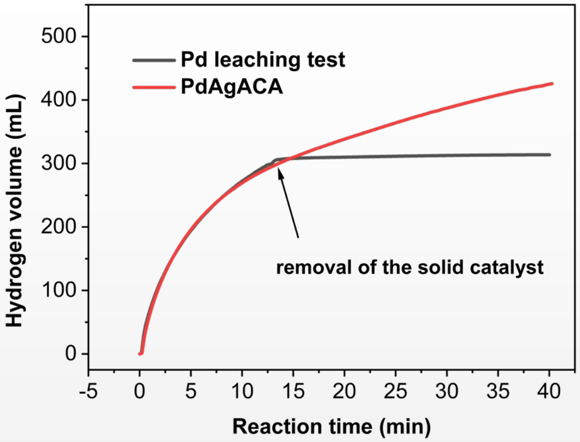
- ☐ We have successfully developed a series of carbon-supported and alternative supports (WSU-1 & WSU-2) supported Pd catalysts which demonstrated a high H_2 uptake and release activity. The synthesized catalysts exhibited a TOF within 2000-14000 h^{-1}.
- ☐ The kinetic data of the best performed Pd/WSU catalysts with the demonstrated good stability were used to calculate the Levelized H_2 delivery cost.

✓ We achieved the M1 of First GNG by demonstrating the fast kinetics of H_2 uptake and release, i.e., TOF > 1000 h^{-1}.

Accomplishments – Excellent Short-Term Stability for H_2 Uptake/Release



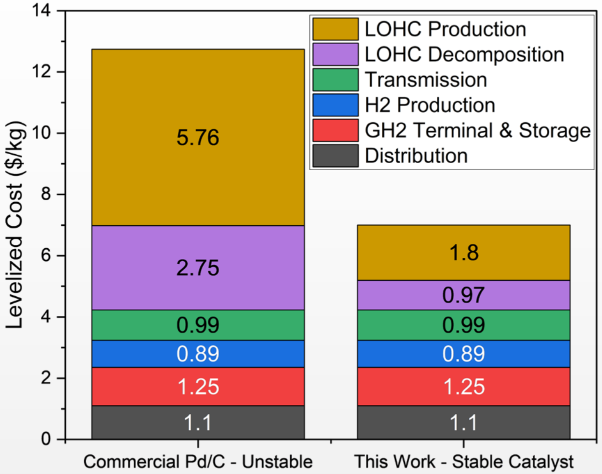


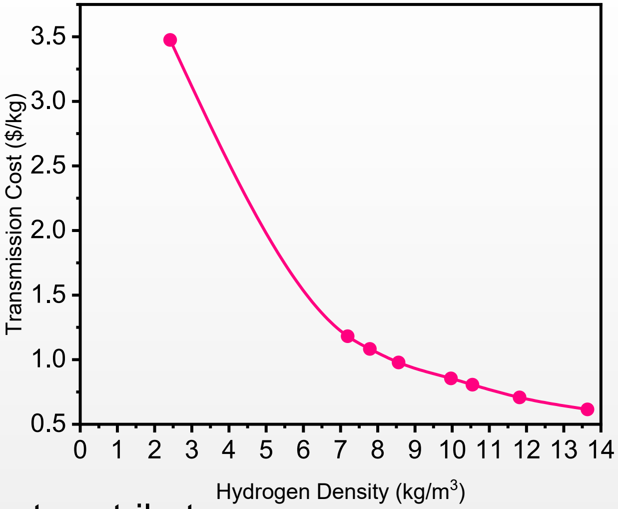


- ❑ We observed that the carbon-supported Pd catalysts are highly active but not stable.
- ❑ Surface modification/functionalization of carbon support enhanced the activity of H_2 uptake and release but doesn't benefit from improving stability.
- ❑ Pd leaching is not a reason for the activity loss/instability.
- ❑ With the alternative supports, both Pd/WSU-1 and Pd/WSU-2 exhibit excellent short-term stability over 10-cycles for H_2 uptake and release, respectively, with the comparable activity compared to the carbon supported Pd catalysts.
  - ✓ We achieved the M2 of First GNG by maintaining 10-cycles stability for H_2 uptake and release.

Accomplishments – Reduced H_2 Levelized Cost of Delivery w.r.t GNG Target

- **Commercial Pd/C – Unstable:** Additional cost of 1% of fresh catalyst per day has been incorporated to maintain activity.
- **This Work – Stable Catalyst :** No additional fresh catalyst is needed.

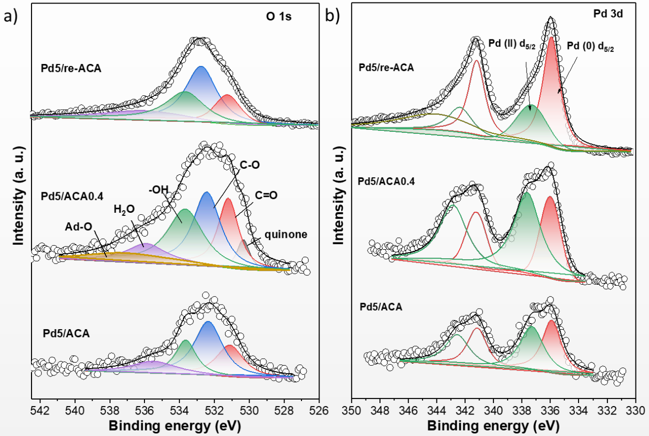


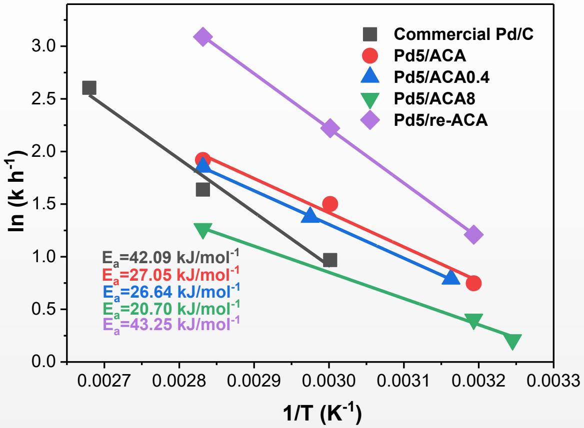


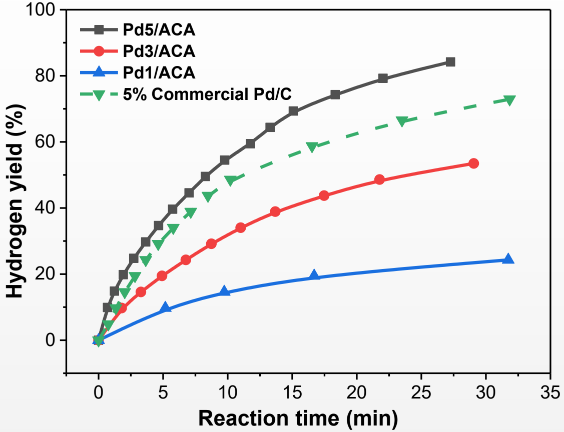
- ☐ Catalyst, transmission, and power costs have been identified as significant contributors.
  - ✓ Pd/WSU with lower Pd loading has been developed to reduce catalyst cost.
  - ✓ Based on sensitivity analysis, the water contents of 90% and 30% contribute to the transmission costs of \$3.47/kg and \$0.99/kg, respectively.
  - ✓ Additional power costs are included at hydrogenation site for electric heating to reduce water content.
  - ✓ We achieved the M3 of First GNG by achieving \$7/kg of H_2 Levelized cost of delivery*.

***https://www.hydrogen.energy.gov/pdfs/20007-hydrogen-delivery-dispensing-cost.pdf – 2020.**

Accomplishments – Improved Pd Dispersion with O-Functional Group on the carbon supports







- Surface O-functional groups limited Pd reduction during the catalyst synthesis process.
  - ❑ Higher Pd dispersion (up to 94.3% improvement) and lower activation energy (up to 50% reduction) were achieved by decorating O-functional groups on the carbon support for the Pd catalyst.

Catalysts	Surface element atomic fraction		
	C (%)	O (%)	Pd (%)
Pd5/re-ACA	96.2	3.21	0.53
Pd5/ACA	94.7	4.77	0.47
Pd5/ACA0.4	89.9	9.13	0.91
Pd5/ACA8	85.9	12.3	1.78

Accomplishments – In-situ ATR-FTIR found Evidence of Stable Bicarbonate Generation

- The C-O stretching peak shows a ‘Blue shift’ from 1403 cm^{-1} to 1397 cm^{-1} during the reaction (0-18 min), which is stable after a half-hour reaction.
- The bicarbonate feature signals at 1350 cm^{-1} show a ‘Red-shift,’ with an increasing wavenumber from 1350 cm^{-1} to 1359 cm^{-1} during the reaction.

☐ Electrons transfer from the C-O bond to bicarbonate species.

☐ Generated bicarbonate species are unstable at the initial stage, and their electron density gets increased with the reaction processing to form more stable bicarbonate.

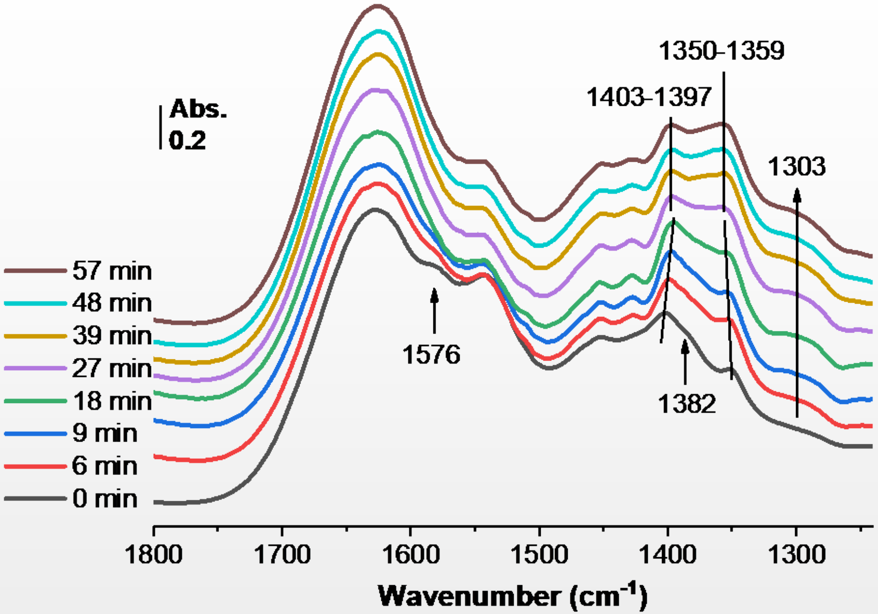
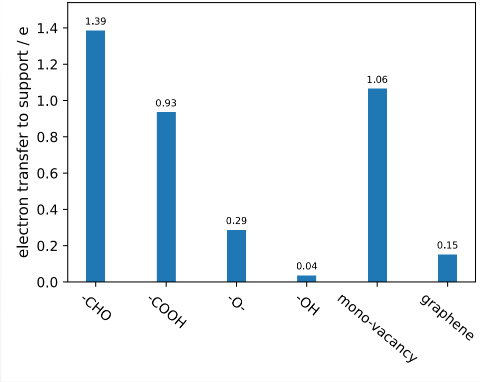
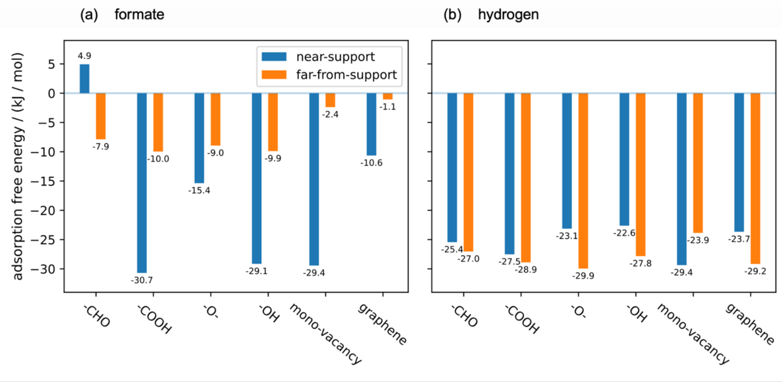
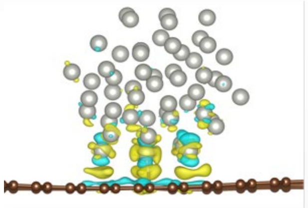


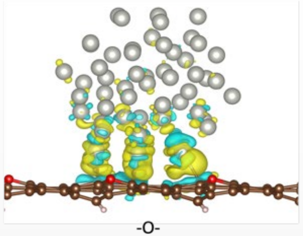
Figure. *in-situ* ATR-FTIR spectra on Pd5/re-ACA catalyst as a function of time recorded after rinsing a 2 M ammonium formate solution to the spectral cell. The reference spectrum was recorded in the air before the rinse.

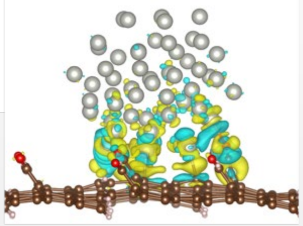
Accomplishments – DFT study Identified Electron Transfer from Pd Metal to Carbon Support

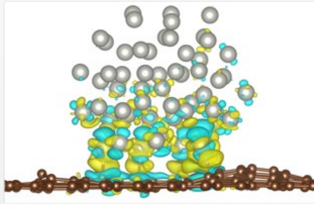





graphene


-O-

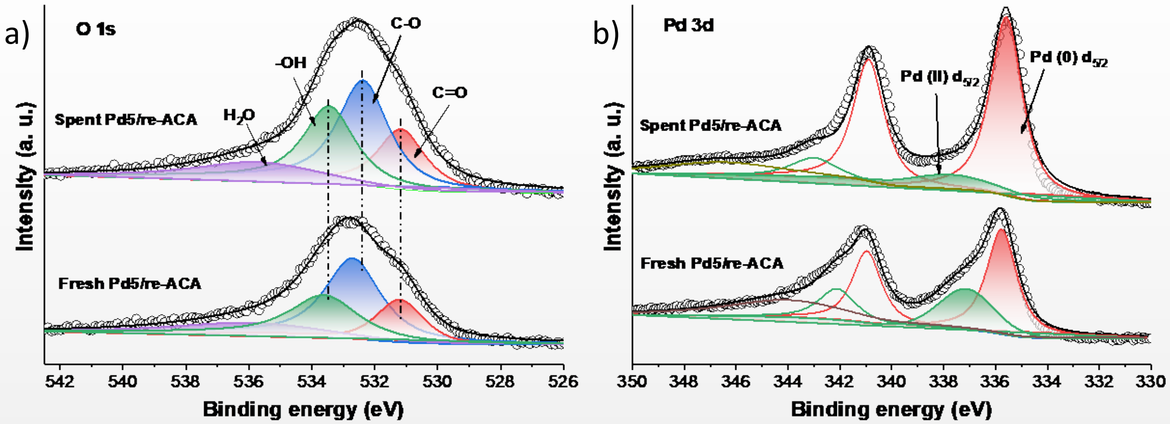

-CHO


vacancy

- ❑ The support effect is much greater for binding sites closer to the support than for sites further away from the support.
- ❑ The support effect is much stronger for formate than hydrogen.
- ❑ Net negative charge transfers from the Pd nanoparticle to the carbon support and leads to:
  - ✓ Partial positive charge on the Pd nanoparticle.
  - ✓ Partial oxidation of the Pd nanoparticle at the interface.

Taking Graphene as a reference, adsorption models has been used, including near-support and far-from-support.

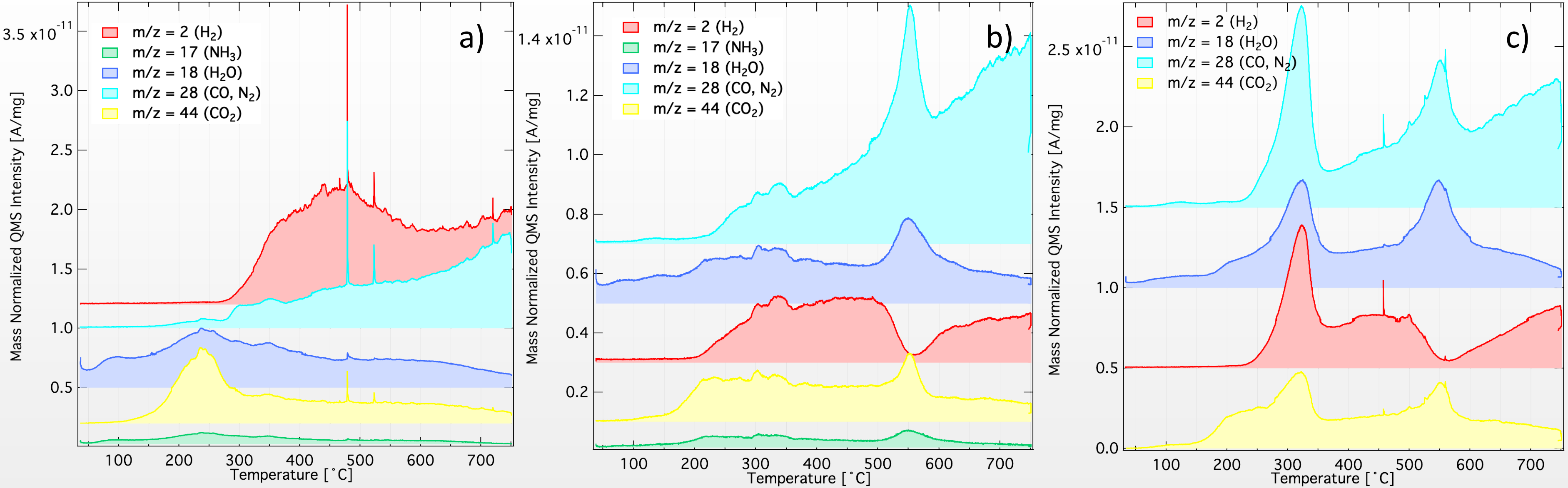
Accomplishments – XPS characterization identified possible Pd on carbon catalyst deactivation mechanism



Catalysts	**Surface Element Atomic Fraction**		
	C (%)	O (%)	Pd (%)
Pd/re-ACA – Fresh	96.2	3.21	0.53
Pd/re-ACA – Spent	94.1	5.10	0.80

- The hydroxyl group fraction on the carbon support increases after formate dehydrogenation, which is attributed to adsorbed O-containing species during the reaction.
- The Pd nanoparticles were easily segregated on the catalyst surface, which is possibly a reason for deactivation.

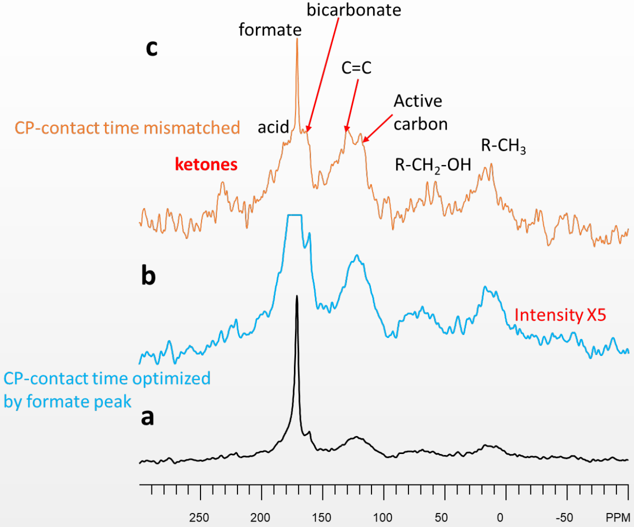
Accomplishments – TPD-MS Characterization identified Strongly Adsorbed Intermediate Species on the Pd on Carbon Catalysts

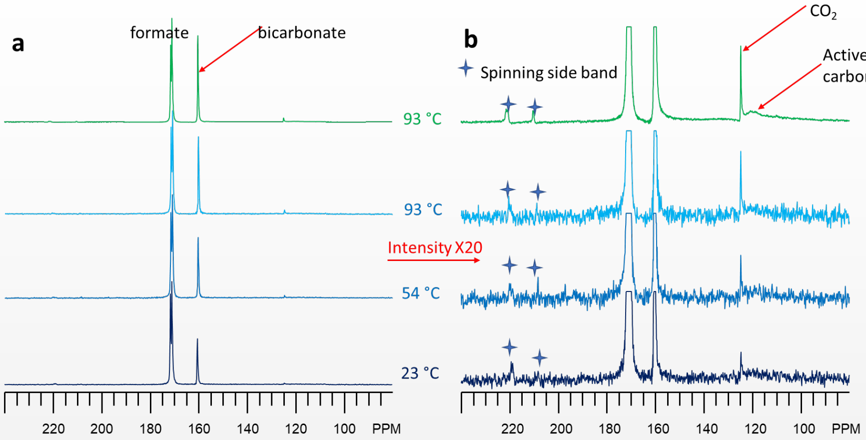


- The bicarbonate ions or intermediates (peak at 335 ^{o}C in TPD-MS) strongly adsorbed on the Pd active sites resulting in deactivation.
- We hypothesized that the bicarbonate ions or intermediates strongly adsorbed on the Pd active sites, poisoning and hindering these Pd sites for catalyzing the dehydrogenation reaction in the next cycle.
- Part of adsorbed species can be cleaned by DI water washing.

Accomplishments – Operando NMR Identified Adsorbed Species on the Pd on Carbon Catalyst Surface

^{1}H-^{13}C cross polarization NMR spectra of formate decomposition over Pd/Ag/AC catalyst (a) optimized CP condition with respect to the formate peak (full intensity spectrum); (b) vertically expanded by 5 times of (a); (c) mismatched conditions with respect to formate but more matched for the other peaks.





Operando ^{13}C single pules NMR spectra of formate to bicarbonate reaction over PdAg/AC catalyst (a) full spectra at various reaction temperatures; (b) intensity vertically expanded by 20 times.

❑ Based on the signature peaks, the intermediate molecule containing oxygen functional groups is likely the surface adsorbed chemical species responsible for the catalyst deactivation.

Reviewer Comments

☐ The focus on catalyst refinements appears premature in the absence of guidance from a baseline TEA. Many key measurements and analyses have not yet been performed. There is no mention of these in the future work statements.

  - ✓ The baseline TEA was acquired with the unstable commercial 5 wt% Pd/AC catalyst. The next generation Pd catalysts have been developed with lower catalyst cost. The kinetic data were used to update the baseline TEA analysis to compare the preliminary H_2 Levelized delivery cost. The *in-situ* ATR-FTIR, TPD-MS and *Operando* NMR characterizations and the DFT calculation have been performed to investigate the formate dehydrogenation reaction mechanism and the catalyst deactivation mechanism, respectively.

☐ There is no meaningful data on the durability of the catalyst. Start generating data on conversion and kinetics (rate) versus cycles or hydrogen produced since the start of the test. That data can tell the project if the catalyst under test has suitable durability. A high-level TEA should give a target that the project must beat.

  - ✓ New efficient next-generation Pd catalysts have been developed with the comparable or better activity compared to the Pd on carbon catalysts. The new catalysts exhibited excellent stability over 10-cycles in H_2 uptake and release. Based on updated TEA analysis, the preliminary H_2 Levelized cost of delivery has been estimated as \$7/kg-H_2.

☐ The project should accelerate the baseline TEA and identify the major cost drivers based on the currently available catalyst and product stream characteristics/impurities.

  - ✓ The major cost drivers in the H_2 Levelized cost of delivery have been identified. The catalyst cost (based on Pd loading), transmission cost (based on water contents in the product stream), and power cost (based on electric heating-assisted water evaporation to reduce water contents) are found to be the significant cost drivers.

Collaborations

Organizations	Team Members	Contributions
Pacific Northwest National Laboratory	Tom Autrey Katarzyna Grubel Kriston Brooks Jian Zhi Hu Mark Engelhard	• Monthly project meetings • Validation of catalyst performance • Nuclear Magnetic Resonance (NMR) Analysis • X-Ray Photoelectron Spectroscopy (XPS)
Lawrence Livermore National Laboratory	Sneha A. Akhade Brandon Wood Thomas Ludwig	• Monthly project meetings • Density Functional Theory (DFT) Calculations
National Renewable Energy Laboratory	Noemi Leick Thomas Gennett	• Temperature Programmed Desorption – Mass Spectrometry (TPD-MS) Analysis
Lawrence Berkeley National Laboratory	Ji Su	• Monthly project meetings • Catalysts synthesis
8 Rivers Capital, LLC.	Navid Rafati Phillip Cross	• Monthly project meetings • Techno-Economic (TEA) Analysis

Barriers and Challenges

- ☐ **Enhancement of Next-Generation Catalysts Activities**
  - ✓ We observed that the carbon-supported Pd catalysts are active but not stable even for short term.
  - ✓ To maintain a good balance between the catalyst activity and stability, the activities of the next-generation materials-supported catalysts can be further enhanced.
- ☐ **Elucidation of Reaction Mechanisms:**
  - ✓ We have demonstrated that the next-generation Pd catalysts are much more stable compared to the carbon supported Pd catalysts. However, an in-depth investigation is required to understand the reaction mechanism.
- ☐ **Lowering the High Cost of Hydrogen Storage:**
  - ✓ It has been found that H_2 Levelized cost of delivery is highly sensitive to catalyst and transmission costs. The catalyst with higher metal loading will results dramatically rise in catalyst cost. The transmission cost is related to water contents in hydrogenation product.
  - ✓ Process integration and optimization should be performed to lower the high levelized H_2 delivery cost

Future Work

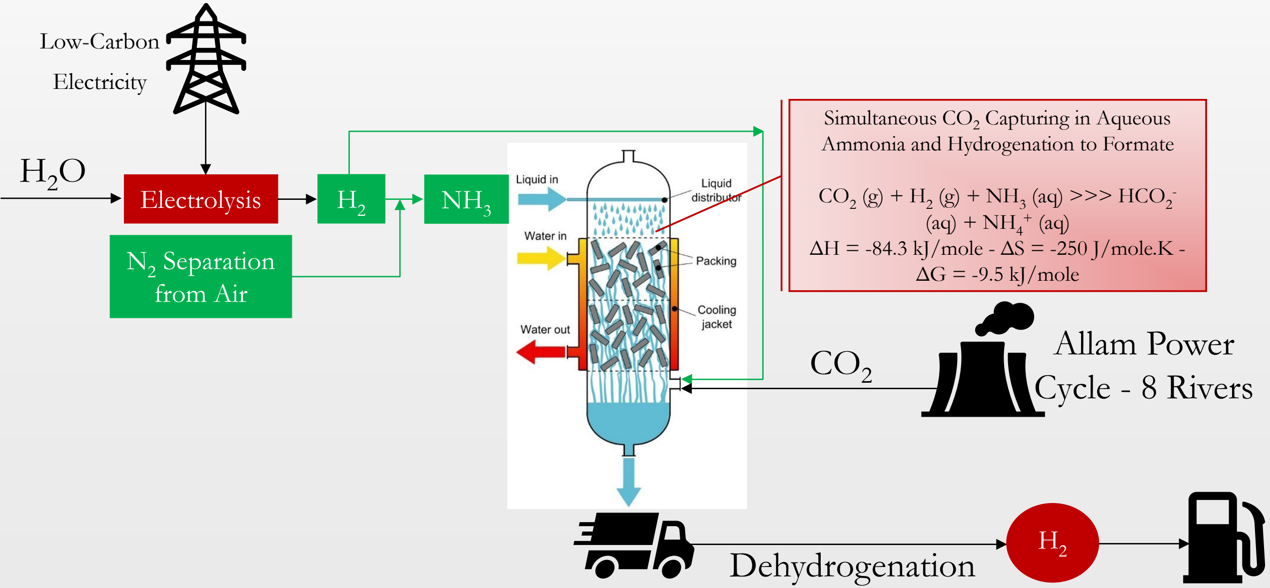
Design, build and optimize a prototype CO_2-to-formate process for reducing the production cost of the formate hydrogen carrier.

☐ Scale up and Synthesize the selected best-performed catalyst.

☐ 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.

☐ Determine the optimized operation conditions in the prototype CO_2-to-formate process.

☐ Demonstrate the preparation of high concentrated ammonium formate using the prototype CO_2-to-formate process.



Simultaneous CO_2 Capturing in Aqueous Ammonia and Hydrogenation to Formate

CO_2 (g) + H_2 (g) + NH_3 (aq) >>> HCO_2^- (aq) + NH_4^+ (aq)

$\Delta H = -84.3$ kJ/mole - $\Delta S = -250$ J/mole.K - $\Delta G = -9.5$ kJ/mole

Summary

- ☐ The carbon-supported palladium catalysts were highly active in H_2 uptake and release but not stable even for short term.
- ☐ The influence of O-functional groups on formate dehydrogenation is complex. Resulting in high Pd dispersion on the support surface and efficiently decreasing the activation energy for dehydrogenation. However, negative charge transfer between the Pd active site and O-functional groups limits the enhancement of the dehydrogenation efficiency.
- ☐ Adsorbed species, Pd surface aggregation, and Pd electronic conditions changes might result in deactivation.
- ☐ Compared to the carbon supported Pd catalysts, the next-generation Pd catalysts on the alternative supports demonstrated excellent stability in H_2 uptake and release with the comparable or better activity to the carbon supported Pd catalysts.
- ☐ In terms of H_2 Levelized delivery cost, the catalyst, transmission, and power costs are identified as the significant cost contributors.

Technical Backup and Additional Information

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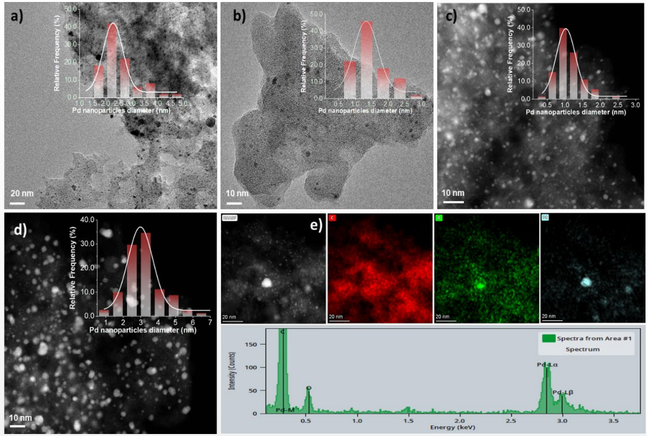
Technical Backup and Additional Information

- Pd nanoparticles are well-dispersed on the carbon support in all self-synthesized catalysts.
- The average diameter of Pd NPs supported on ACA is ~2.5 nm, and those of Pd5/ACA0.4 and Pd5/ACA8 catalysts are ~1.5 nm and ~1.2 nm.
- The smaller Pd nanoparticles might result in higher Pd dispersion in Pd5/ACA catalysts (30.0% of Pd5/re-ACA and 45% of Pd5/ACA8, respectively).
- The EDX results reveal the existence of C, O, and Pd elements. O atoms and Pd NPs are homogeneously dispersed on the carbon support.
- Pd was loaded in the form of single atoms and the more Pd single atoms were generated with a higher concentration of HNO_3 treatment, indicating O-functional groups are beneficial to improve the Pd dispersion with more small nanoparticles, nanoclusters, and single-atoms.
- The lattice distance of the particles is 0.223 nm, corresponding to Pd (111) structure.

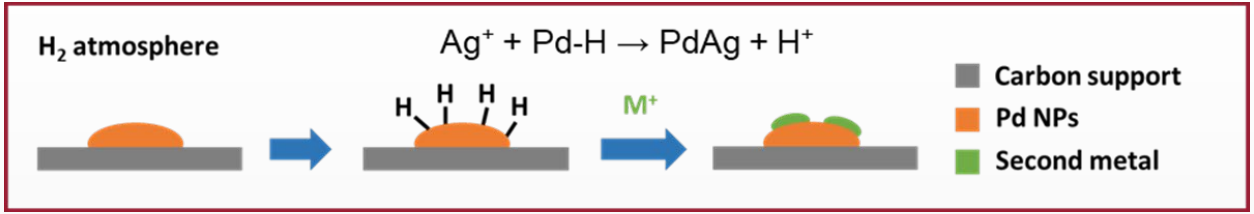


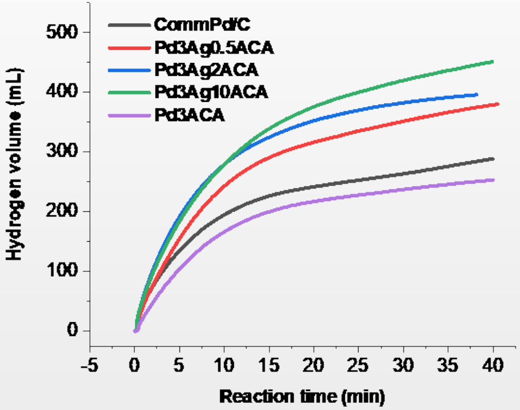
Catalysts	TOF (h^{-1})
Commercial Pd/C	5246
Pd5/NC-HNO3	13103
Pd2.5/NC-HNO3	17078
Pd5/NC-NaOH	5511
Pd2.5/NC-NaOH	9775
Pd5/ACA	3122
Pd5/ACA0.1	2601
Pd5/ACA0.4	3462
Pd5/ACA1.6	3059
Pd5/re-ACA	13511
Pd3Ag3/ACA	11634#
Pd3Ag10/ACA	21229#

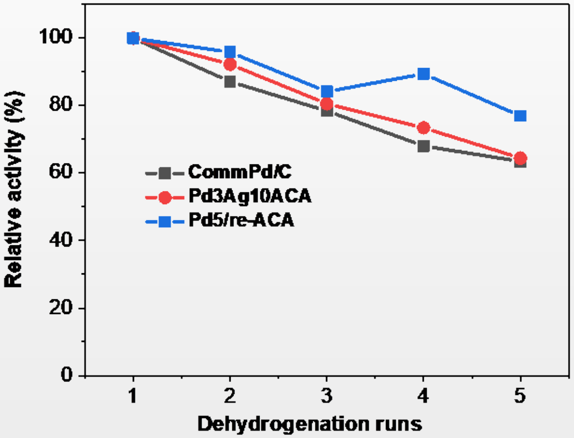
A series of self-synthesized Pd on carbon catalysts has been developed with fast kinetics of H_2 uptake and release.

TOF number were calculated in first 10 min, (mole of H_2)/(mole of Pd*Pd dispersion*time).
#Estimate that Pd was the active site for dehydrogenation.

Technical Backup and Additional Information







- ❑ Optimized bimetallic Pd-Ag/ACA catalyst shows much improved dehydrogenation performance compared with the commercial Pd/C catalyst
- ❑ We developed the bimetallic catalysts by identifying the metal species with the reduction potential that can be used to synthesize Pd-based catalyst through optimized galvanic replacement method.
- ❑ The reduction potential of second metal species should be < Pd.
- ❑ Carbon-supported catalysts doesn’t demonstrate good stability.

Technology Transfer Activities

An agreement between the **Washington State University** and **8 Rivers Capital, LLC**, has been signed on **February 5th, 2021** to seek the protection of Intellectual Property (IP) for potential patent licensing.

Publications and Presentations

Published Papers:

Dong, Zhun, Ahmad Mukhtar, and Hongfei Lin, Heterogeneous Catalysis on Liquid Organic Hydrogen Carriers. **Topics in Catalysis** 64, no. 7 (2021): 481-508.

Manuscripts in preparation:

Zhun Dong, Ahmad Mukhtar, Thomas Ludwig, Sneha A. Akhade, Shin Young Kang, Brandon Wood, Katarzyna Grubel, Mark Bowden, Tom Autrey, Hongfei Lin, An efficient Pd-based catalyst for ammonium formate dehydrogenation: the effect of oxygen functional groups (in preparation).

Zhun Dong, Ahmad Mukhtar, Thomas Ludwig, Sneha A. Akhade, Wenda Hu, Jianzhi Hu, Noemi Leick, Thomas Gennett, Tom Autrey, Hongfei Lin, Efficient carbon-supported Pd-Ag bimetallic catalysts for ammonium formate dehydrogenation by tuning the surface alloy compositions (in preparation).

Presentations:

Hongfei Lin, Tom Autrey, Katarzyna Grubel, Kriston Brooks, Jian Zhi Hu, Mark Engelhard, Sneha A. Akhade, Brandon Wood, Thomas Ludwig, Noemi Leick, Thomas Gennett, The Role of Pd-based Heterogeneous Catalysts in the Application of Ammonium Formate Hydrogen Carrier, **ACS Spring 2022 Conference in San Diego, CA.**