WASHINGTON STATE UNIVERSITY

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

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DOE Hydrogen Program
2023 Annual Merit Review and Peer Evaluation Meeting

AMR Project ID: ST217

DOE HyMARC Program 2023 Annual Merit Review and Peer Evaluation Meeting

Project Goal

- Develop efficient hydrogenation catalysts for the hydrogenation of ammonium bicarbonate with good long-term stability (>25 successive runs without activity loss) and catalyst synthesis scalability (prepare >10 grams of the best-performed hydrogenation catalyst).
- Design, build and optimize a prototype, laboratory-scale CO_2-to-formate process, which integrates CO_2 capture and hydrogenation with aqueous ammonia.
- Demonstrate the economics for the simulated CO_2-to-formate process with a >30% reduction in the production cost of the ammonium formate over the market-based baseline performance data.

Project Overview

Timeline

Project Start Date: 02/12/2020
Project End Date: 09/30/2024*

**Project continuation and direction annually determined by DOE.* —

Budget

DOE Funding received in FY22: $303,169
DOE Funding received to date: $808,740
($643,141 federal funds and $165,599 cost share by WSU and 8Rivers)

Barriers

- ☐ Catalyst Activity and Stability
- ☐ Process Intensification
- ☐ Process Economics

Partners

- ☐ Partners:
  - ➢ Washington State University
  - ➢ 8Rivers Capital
- ☐ Collaborators:
  - ➢ Pacific Northwest National Laboratory
  - ➢ Lawrence Livermore National Laboratory
  - ➢ National Renewable Energy Laboratory

Relevance/Potential Impact

Barriers	Potential Impacts
Catalyst Activity and Stability	Regarding H_2 Levelized delivery cost, the catalyst, transmission, and power costs are identified as the significant cost contributors. Therefore, developing highly active and stable hydrogenation catalysts will result in less utilization of noble metal and enable the production of concentrated ammonium formate solutions from ammonia-captured CO_2, thus reducing the water-drying cost and further decreasing the transmission cost.
Process Intensification	Integrating CO_2 capture with hydrogenation to produce ammonium formate from CO_2 could avoid the energy penalties associated with the desorption of CO_2 from aqueous ammonia.
Process Economics	The prototype CO_2-to-formate process has been designed and built to collect kinetic data for techno-economic analysis. Leveraging the existing infrastructure of the industrial partner has the potential to improve the overall process economics.

Specific objectives for the current year:

- ☐ Develop and synthesize the next-generation hydrogenation catalyst
- ☐ Design, build, and optimize the prototype CO_2-to-formate process
- ☐ Perform techno-economic analysis for the simulated large-scale CO_2-to-formate process

Approach

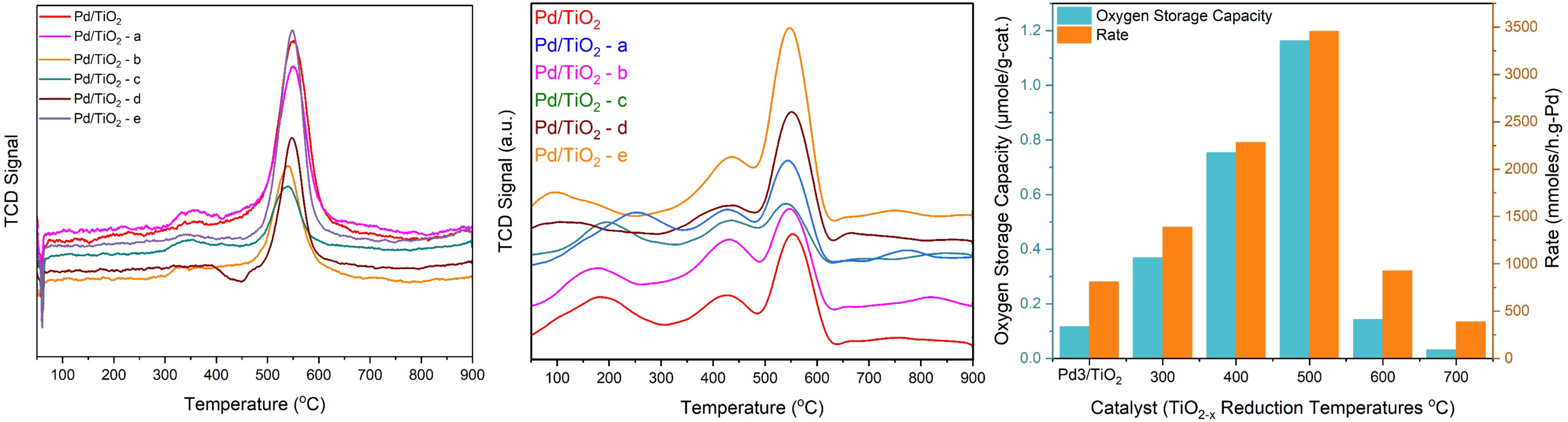
Technical Approach to Deliver Milestones and Meet Project Goals:

- ❑ Our approach is to achieve efficient H_2 storage, transport, and delivery using a two-way, ammonium formate-based liquid organic hydrogen carrier with highly active and robust palladium (Pd) catalysts.
  - ➢ Catalyst for Hydrogen Uptake: Reducible metal oxide-supported Pd catalysts have strong metal-support interactions, facilitating H_2 spillover from metal to support, which could enhance the hydrogenation kinetics. In addition, the (sub)surface oxygen vacancies (O_v) on metal oxide support can be tuned to stabilize and mobilize Pd nanoparticles and reaction intermediates, enhancing the catalyst's activity and stability.
  - ➢ Catalyst for Hydrogen Release: The dehydrogenation process is facilitated by the development of carbon-supported bimetallic catalysts with tunable metal surface electronic properties, resulting in an enhanced H_2 release rate.
  - ➢ Process Integration: Integration of CO_2 capture and hydrogenation to produce ammonium formate could leverage the existing infrastructure of our industrial partner and thus may significantly decrease the production cost of ammonium formate.

Accomplishments and Progress
Response to Previous Year Reviewer's Comments

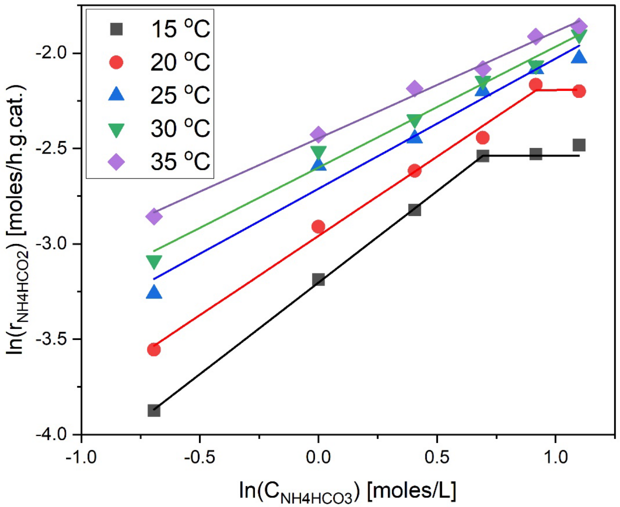
This project was not reviewed for FY2022.

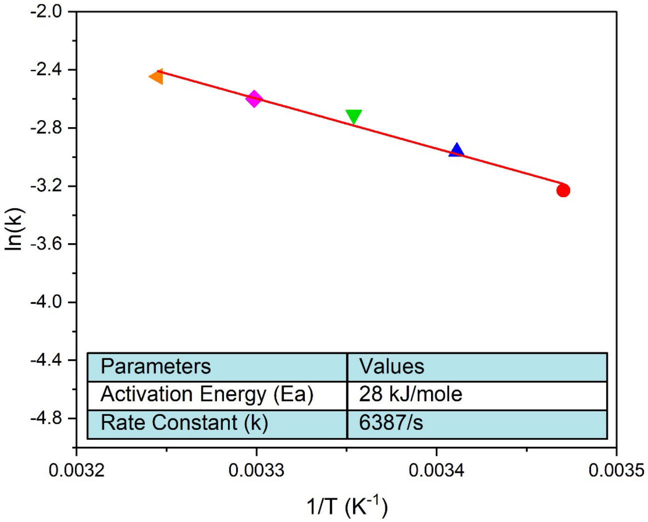
Accomplishment: Correlated oxygen storage capacities of TiO_2 supports with hydrogenation kinetics



- H_2 Temperature Programmed Reduction (TPR): The Pd/TiO_2-c catalyst sample with the smallest H_2 TPR peak at ~550°C indicates the presence of the highest amount of O_v on TiO_2 or the highest Pd/PdO_x ratio.
- H_2 Temperature Programmed Desorption (TPD): The Pd/TiO_2-c catalyst sample with the most miniature H_2 TPD peaks at >150°C also indicates the presence of the highest amount of O_v.
- Oxygen Storage Capacity (OSC) vs. Hydrogenation Reaction Rate: The role of O_v in mobilizing and stabilizing bicarbonate ions was found to be prominent. H_2 might spill over the TiO_2 support after being dissociated at the Pd surface. A positive correlation of the oxygen storage capacities of the TiO_2 supports with the ammonium bicarbonate hydrogenation rates was observed.

Accomplishment: Acquired the key kinetic parameters of ammonium bicarbonate hydrogenation reaction over the best-performed catalyst



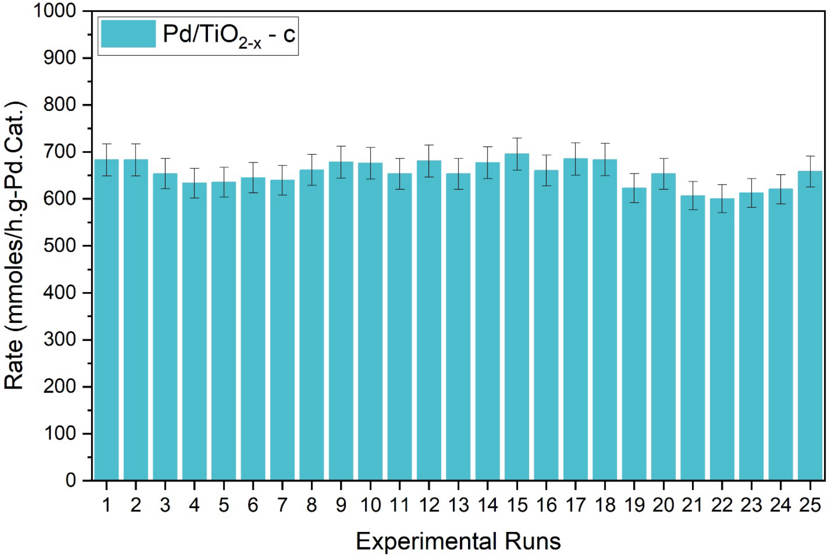


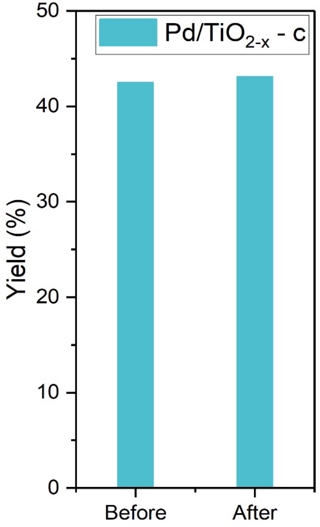
Parameters	Values
Activation Energy (Ea)	28 kJ/mole
Rate Constant (k)	6387/s

Reaction Conditions: Catalyst loading (50 mg), H_2 partial pressure (500 psi), reaction time (10 minutes), and stirring speed (350 rpm).

- The ammonium bicarbonate hydrogenation was confirmed to be the first-order reaction. However, at high concentrations, the reaction order was shifted to zero order, probably due to the limited catalyst loading amount.
- The activation energy of hydrogenation was significantly reduced to 31 kJ/mole over the best-performed Pt/TiO_2-c catalyst compared to that on the commercial catalyst Pd/C (~54 kJ/mole).

Accomplishment: Demonstrated the good stability of the best-performed hydrogenation catalyst



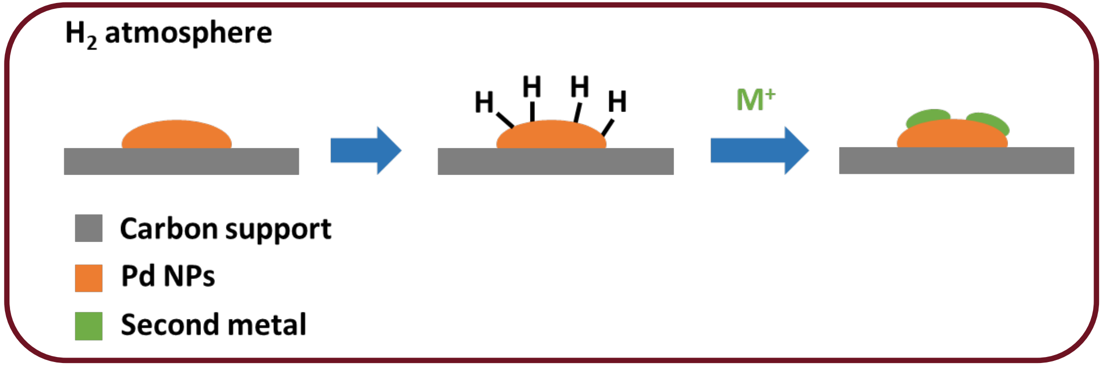


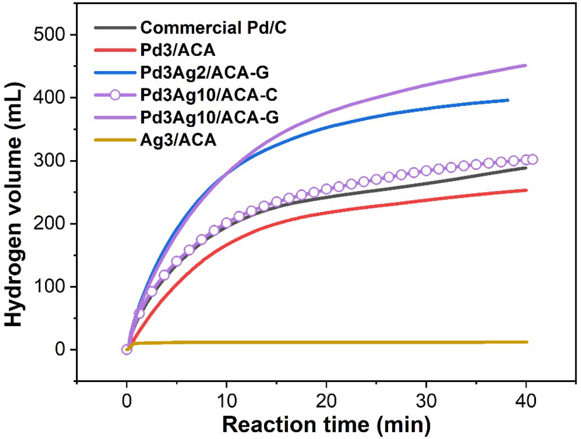
	Atomic Ratios	
Pd/TiO$_2$ - c	Pd	Ti
Fresh	1.97	27.26
1st Run	2.71	27.12
5th Run	2.65	25.62

- ☐ The surface Pd to Ti atomic ratio slightly increased after reactions.

- ☐ The best-performed Pd/TiO$_2$ catalyst for hydrogenation maintained its activity over 25 successive experimental runs. Reaction Conditions: H$_2$ partial pressure (500 psi), reaction time (10 minutes), and stirring speed (350 rpm).
- ☐ No increase in the yield of ammonium formate was observed after removing the solid Pd/TiO$_2$ catalyst, indicating that the possible Pd ions in the solution, if present due to catalyst leaching, should not be active.

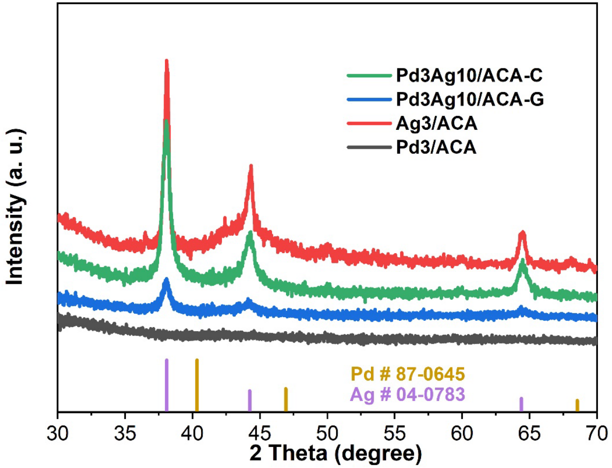
Accomplishment: Developed a novel method to synthesize Pd-Ag bimetallic catalysts with enhanced dehydrogenation performance

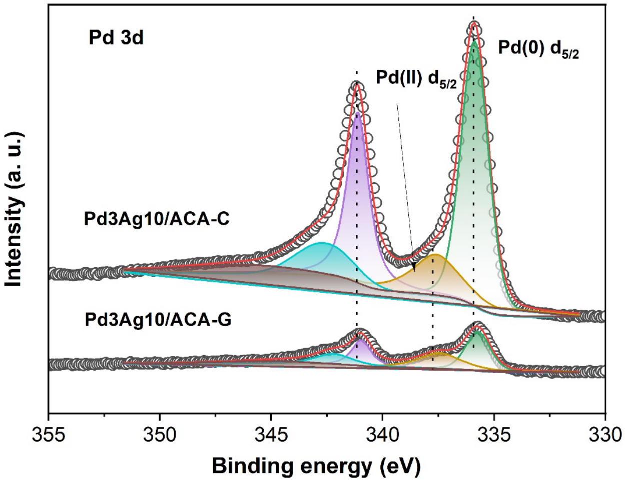


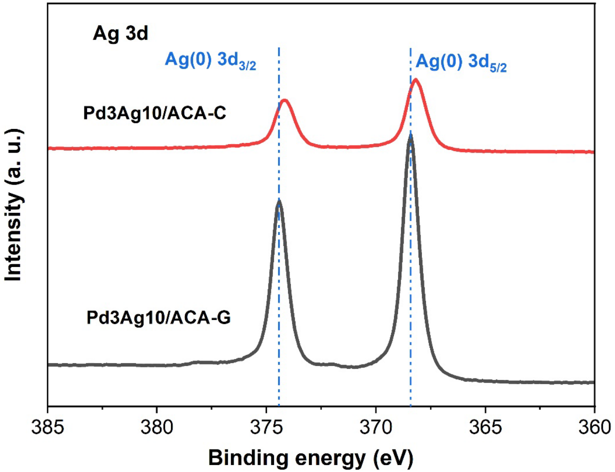


- ❑ A novel galvanic replacement method has been developed to synthesize carbon-supported Pd-Ag bimetallic nanoparticles (NPs) catalysts which showed enhanced ammonium formate dehydrogenation performance compared to the catalyst prepared by the conventional co-reduction method and the commercial Pd/C.
- ❑ With more surface-decorated Ag species, the interaction between Pd-Ag species was enhanced, leading to higher activity.

Accomplishment: Elucidated the surface electronic structure of the Pd-Ag bimetallic catalyst

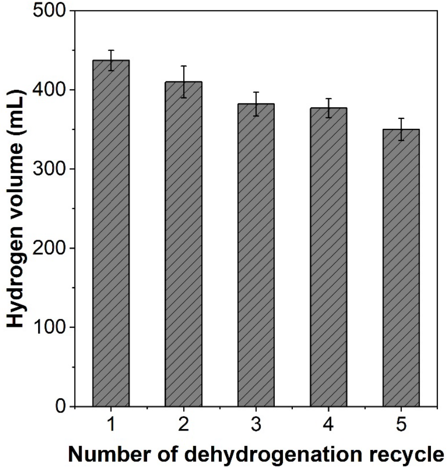


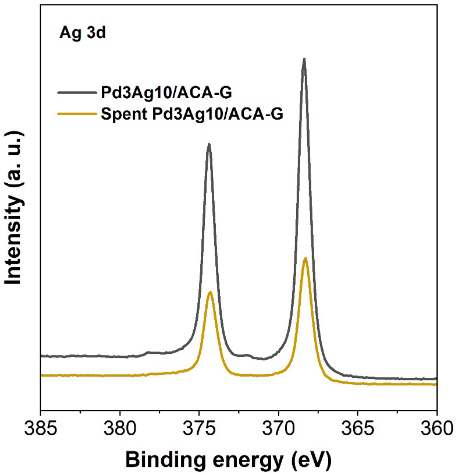


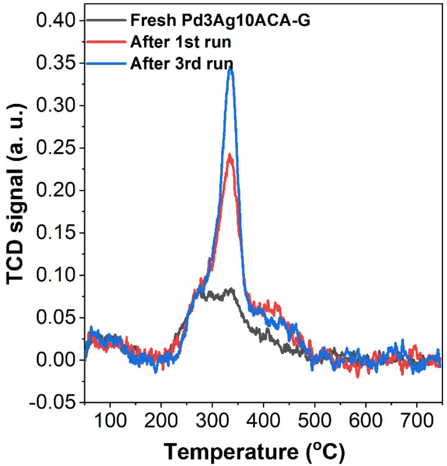


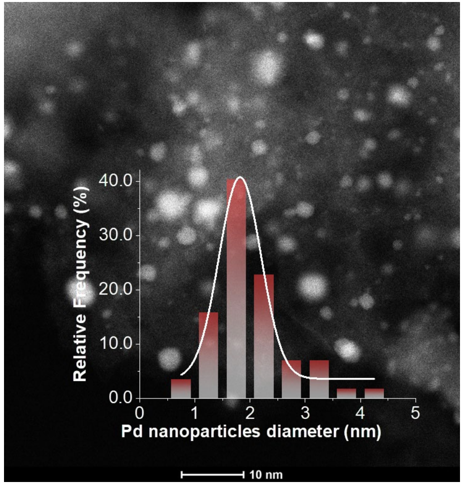
- ❑ X-Ray Diffraction (XRD): No noticeable peaks related to metallic Pd species are observed, suggesting Pd nanoparticles were highly dispersed on the carbon support.
- ❑ X-Ray Photoelectron Spectroscopy (XPS): The Pd^0 species are observed to be dominant over the Pd3Ag10/ACA-G catalyst, suggesting enriched electrons on the catalyst surface. Likewise, the Ag 3d spectra display that surface Ag is also in the metallic state.

Accomplishment: Identified possible mechanisms leading to catalyst deactivation



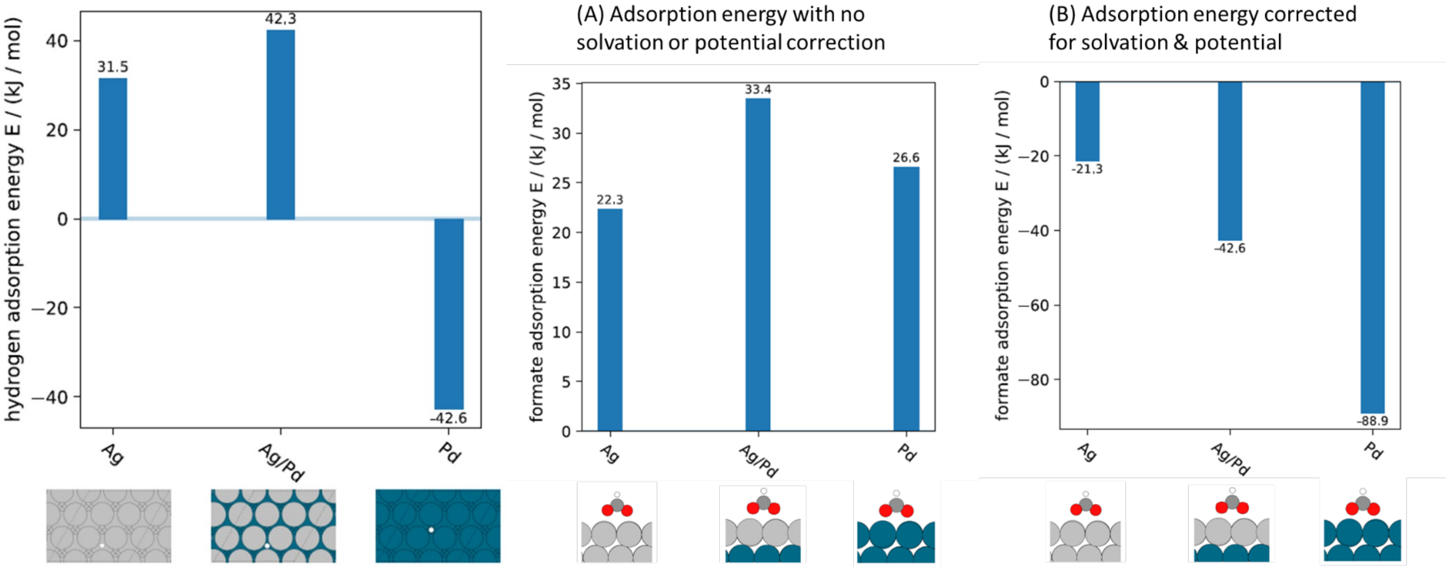






- ☐ The stability test revealed that the activity of the Pd-Ag on carbon catalysts gradually decreased after five successive runs.
- ☐ Lower peak intensity of Ag in the XPS spectra indicates a decrease in the surface decorated Ag species on the spent catalyst.
- ☐ The increase in decomposition temperature from 250 °C to 350 °C suggests that the surface carboxylate species may negatively impact the dehydrogenation activity.
- ☐ TEM image indicates that the Pd particle size increased from 1.6 to 2.0 nm after the reaction.

Accomplishment: Elucidated ammonium formate dehydrogenation reaction mechanism on Pd-Ag via DFT calculations



- The H_2 adsorption energy on Pd (111) surface is -42.6 kJ/mol, much lower than that on Ag (111) surface (31.5 kJ/mol), indicating strong binding of H_{ad} to the Pd than Ag surface.
- The formate adsorption is much stronger on Pd (111) surface (-88.9 kJ/mol), weaker on Ag (111) surface (-21.3 kJ/mol), and intermediate in Pd/Ag surface alloy (-42.6 kJ/mol).

Collaboration and Coordination

Organizations	Team Members	Roles
Pacific Northwest National Laboratory	Tom Autrey Katarzyna Grubel Kriston Brooks Jian Zhi Hu Mark Engelhard	• Attend monthly project meetings • Validate catalyst performance results • Perform Nuclear Magnetic Resonance (NMR) analysis • Perform X-Ray Photoelectron Spectroscopy (XPS) analysis
Lawrence Livermore National Laboratory	Sneha A. Akhade Brandon Wood Thomas Ludwig	• Attend monthly project meetings • Perform Density Functional Theory (DFT) calculations
National Renewable Energy Laboratory	Noemi Leick Thomas Gennett	• Perform Temperature Programmed Desorption – Mass Spectrometry (TPD-MS) analysis
8 Rivers Capital, LLC.	Phillip Cross Joe Weiner	• Attend monthly project meetings • Perform Techno-Economic Analysis (TEA)

Proposed Future Work

- ☐ Remainder of Budget Period 2:
  - ✓ Optimize the prototype CO_2-to-formate process to produce highly concentrated ammonium formate solutions.
  - ✓ Perform TEA to demonstrate the simulated large-scale CO_2-to-formate process could lower the overall production cost of ammonium formate by 30% compared to the commercial process as a baseline.
- ☐ Proposed work for Budget Period 3:
  - ✓ Design, build, and optimize a prototype formate-to-power process and perform a detailed techno-economic analysis (TEA) of the whole process to validate the final project goal, i.e., the Levelized H_2 delivery cost using ammonium formate as a two-way H_2 carrier is comparable or lower than that of using commercial high-pressure (700-bar) tube trailers.

Any proposed future work is subject to change based on funding levels

Project Summary

- We have developed a novel galvanic replacement method to synthesize carbon-supported Pd-Ag bimetallic catalysts for ammonium formate dehydrogenation. The best-performed Pd-Ag bimetallic catalyst displayed a two times higher kinetic rate than the commercial Pd/C catalyst. A thorough investigation of reaction mechanisms has been performed with characterizations and DFT calculations.
- We have optimized the synthesis methods and prepared >10 grams of the best-performed Pd on TiO_2 catalysts with tunable oxygen vacancies, exhibiting high activity in ammonium bicarbonate hydrogenation. Besides, we have demonstrated this catalyst's good long-term stability with 25 successive runs without activity loss.
- We have developed and built the prototype CO_2-to-formate process by integrating CO_2 capture and hydrogenation with aqueous ammonia solutions. We are optimizing the operating conditions to produce highly concentrated ammonium formate solution, and the techno-economic analysis of the simulated large-scale CO_2-to-formate process is an ongoing task.

Technical Backup and Additional Information

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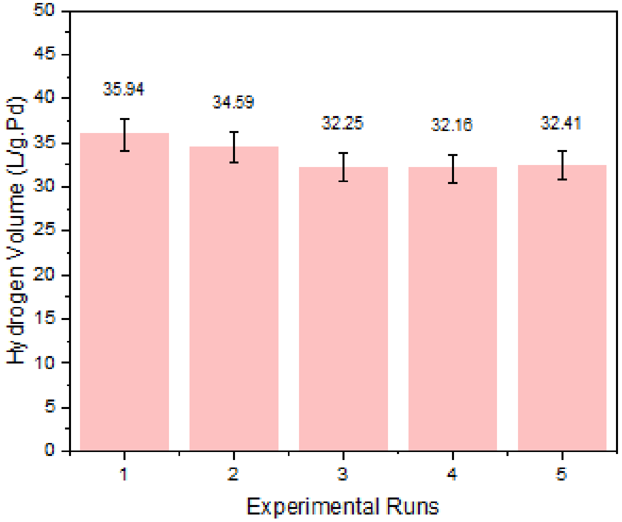
Technical Backup and Additional Information



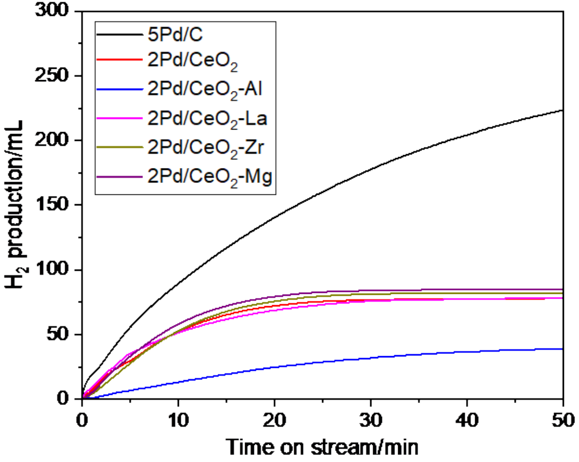
- Pd3/TiO2-c demonstrated short-term stability in the dehydrogenation of ammonium formate

Reaction conditions: ammonium formate (1M, 20 mL), temperature (80 °C), reaction time (40 minutes per run), and stirring speed (350 rpm).

Ammonium bicarbonate hydrogenation

Catalyst	**Activity (mol Formate/ mol-Pd.h)**
5Pd/C	167.5
2Pd/CeO_2	523.3
2Pd/CeO_2-Al_2O_3 (9:1)	168.4
2Pd/CeO_2-La_2O_3 (9:1)	381.4
2Pd/CeO_2-MgO (9:1)	571.1
2Pd/CeO_2-ZrO_2 (9:1)	471.3

Ammonium formate dehydrogenation



- 2Pd/CeO_2-MgO gave better activity in both hydrogenation and dehydrogenation than the reference 2Pd/CeO_2 catalyst.

Technology Transfer Activities

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

Publications and Presentations

- Dong, Zhun, Ahmad Mukhtar, Thomas Ludwig, Sneha A. Akhade, ShinYoung Kang, Brandon Wood, Katarzyna Grubel, Mark Engelhard, Tom Autrey, and Hongfei Lin. “Efficient Pd on carbon catalyst for ammonium formate dehydrogenation: Effect of surface oxygen functional groups.” **Applied Catalysis B: Environmental** 321 (2023): 122015.

- Ahmad Mukhtar, Sidra Saqib, Jangam Ashok, Zhun Dong, Mark Bowden, Mark Engelhard, Katarzyna Grubel, Tom Autrey, Hongfei Lin, “Highly Active and Stable Pd Nanoparticles Supported Over Defective Mesoporous TiO_{2-x} for Bicarbonate Hydrogenation: Role of H2 Spillover and Oxygen Vacancies”, Submitted.

- Zhun Dong, Ahmad Mukhtar, Thomas Ludwig, Sneha A. Akhade, Wenda Hu, Jian Zhi Hu, Katarzyna Grubel, Mark Engelhard, Tom Autrey, Hongfei Lin, “Carbon-supported Pd-Ag bimetallic catalyst with exceptional activity for ammonium formate dehydrogenation”, Submitted.