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

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DOE Hydrogen Program
2024 Annual Merit Review and Peer Evaluation Meeting

AMR Project ID: ST217

DOE HyMARC Program 2024 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 FY23: $214,153
DOE Funding received to date: $814,680
($649,081 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

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 dewatering cost and further decreasing the transmission cost.
Process Intensification	Integrating CO_2 capture with hydrogenation to produce ammonium formate from ammonia-captured 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 the techno-economic analysis (TEA). 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 mobilize Pd nanoparticles and stabilize reaction intermediates, enhancing the catalyst's activity and stability.
  - ➢ 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.

Approach: Safety Planning and Culture

Hydrogen Safety Plan Compliance and Safety Culture in Reversible Liquid Hydrogen Carrier – Ammonium Formate (RLHC-AF) Project

Safety Plan Submission to HSP

Requirement Status:

- Required and Submitted

HSP Feedback Actions:

- Enhanced Process Flow Diagrams for improved safety shutoff visibility.
- Adopted HSP's recommended risk mitigation strategies for high-pressure testing.
- Initiated quarterly HSP reviews for ongoing safety oversight.

Safety Culture in the RLHC-AF Project

Prioritization of Safety & Hazard Analysis:

- Implemented a comprehensive Hazard Identification and Risk Assessment (HIRA) protocol.
- Executed full-scale safety audits prior to initiating any experiments.

Response to Incidents & Near-Misses:

- Established a transparent incident reporting system.
- Conducted quarterly safety drills tailored to previous near-miss scenarios.

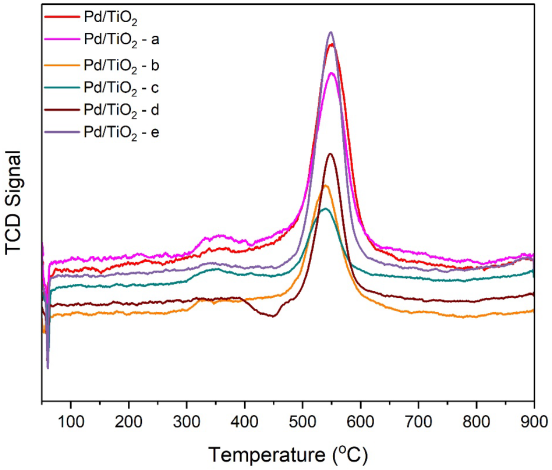
Best Practices & Lessons Learned Incorporation:

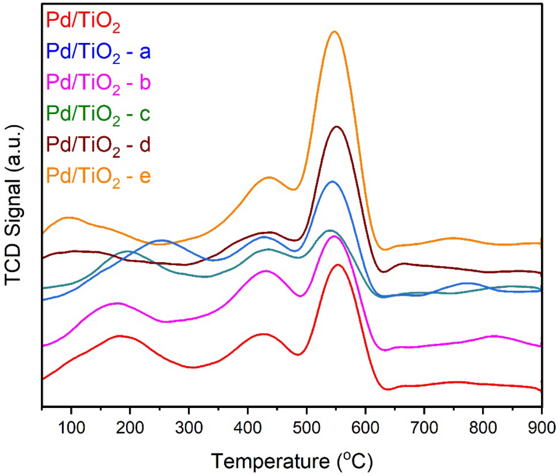
- Engaged in continual safety training sessions aligned with HSP guidelines.
- Upgraded to industry-leading safety equipment based on recent case studies.

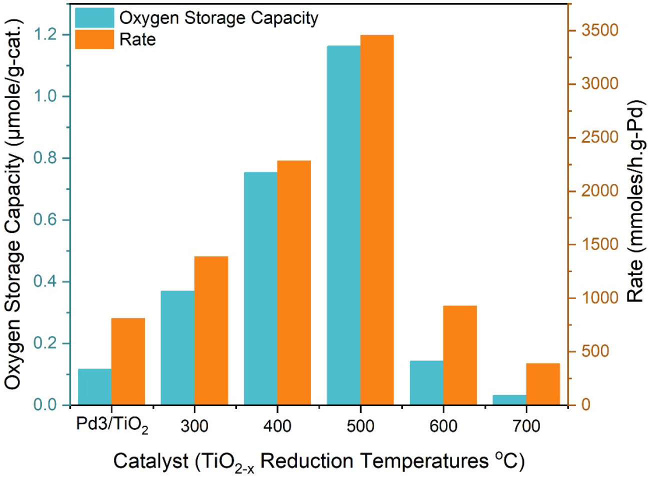
Accomplishments and Progress
Response to Previous Year Reviewer's Comments

This project was not reviewed for FY2022.

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

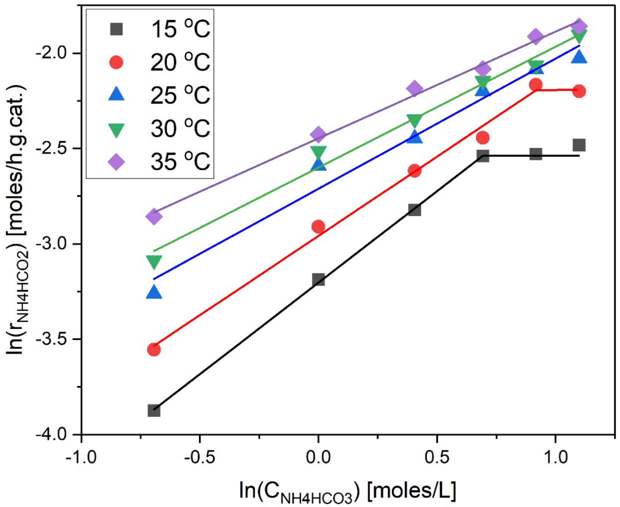


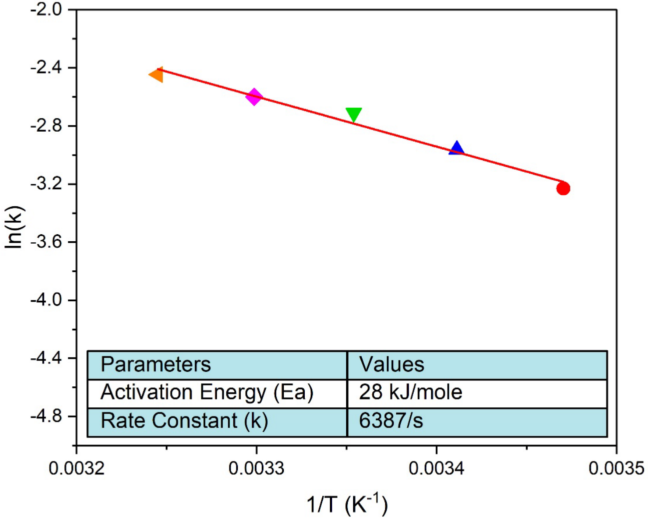




- **H_2 Temperature Programmed Reduction (TPR):** The Pd/TiO_2-c catalyst sample with the smallest H_2-TPR peak at ~550°C indicates the presence of the highest amount of O_v on TiO_2 or the highest Pd/PdO_x ratio.
- **H_2 Temperature Programmed Desorption (TPD):** The Pd/TiO_2-c catalyst sample with 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 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



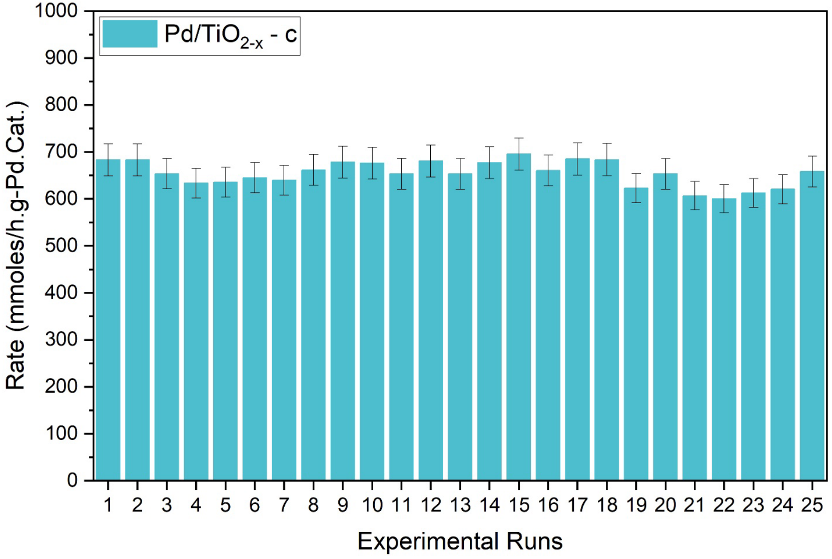


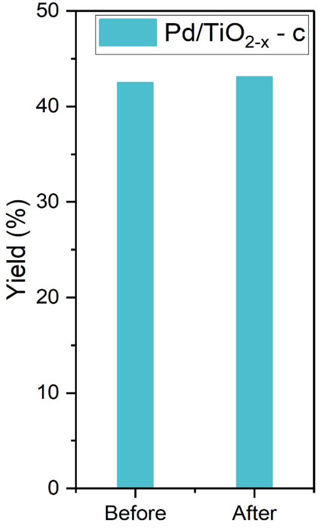
Parameters	Values
Activation Energy (Ea)	28 kJ/mole
Rate Constant (k)	6387/s

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 in bicarbonate. 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 28 kJ/mol 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

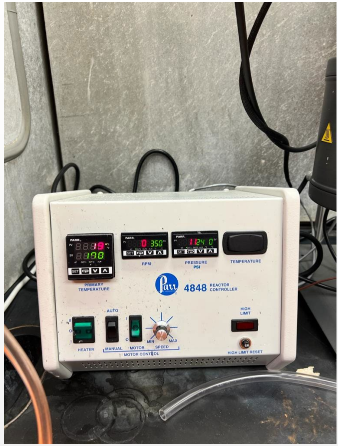




	Atomic Ratios	
Pd/TiO$_2$ - c	Pd	Ti
Fresh	1.97	27.26
1st Run	2.71	27.12
5th Run	2.65	25.62

- ❑ The best-performed Pd/TiO$_2$-c catalyst for hydrogenation maintained its activity over 25 successive experimental runs. However, the surface Pd to Ti atomic ratio slightly increased after reactions. 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 be inactive.
- ❑ The catalyst synthesis is scalable. We synthesized > 50 g of catalyst for the following experiments.

Accomplishment: Demonstrated the prototype CO_2-to-formate process to produce ammonium formate using pressurized CO_2 and H_2 gases



Controller

Reactor

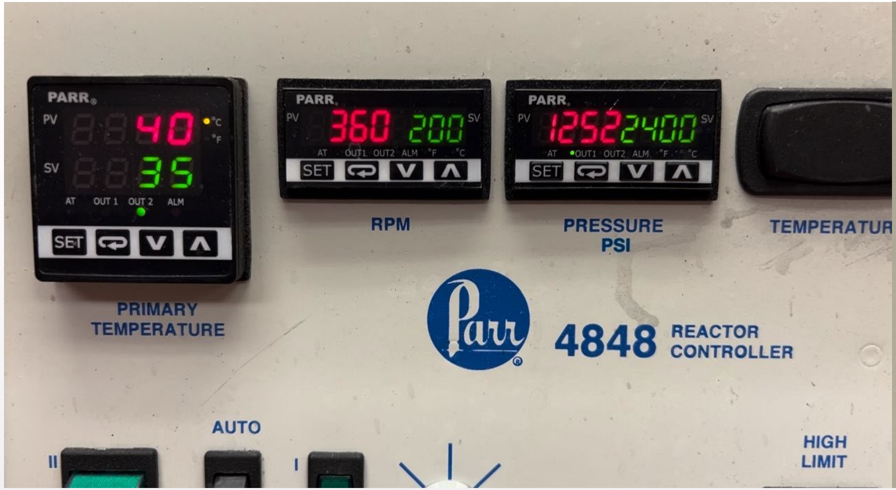
Liquid CO_2

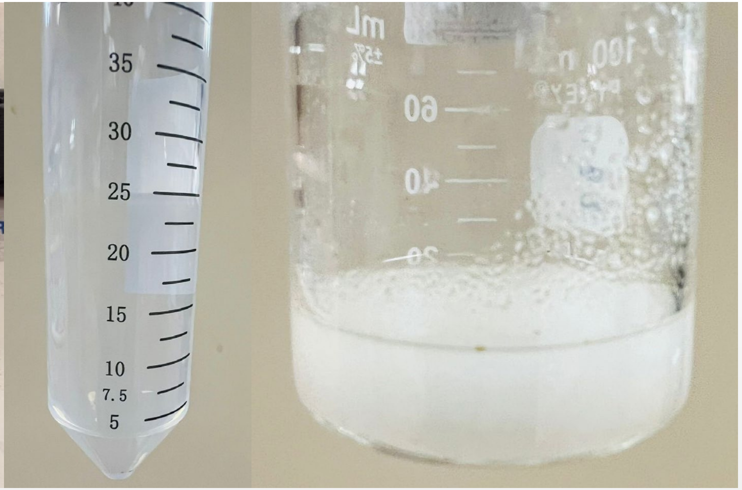
Pressure (psi) (H_2 + CO_2)	Formate Conc. (M)
300 + 700	0.037
500 + 500	0.091
700 + 300	0.786

Reaction Conditions: Ammonia (aq. 30 wt.%, ~7M, 20 mL), catalyst loading (200 mg), time (1 hour), temperature (30 ^{o}C), and stirring speed (350 rpm).

- "One-Pot" simultaneous CO_2 capture and hydrogenation produced ammonium formate but only at low yields.
- The yield of ammonium formate was sensitive to H_2 partial pressure.
- The maximum operation pressure for the 100-mL Parr reactor is 1500 psi, limiting the use of the supercritical CO_2 for hydrogenation. (to maintain supercritical CO_2 state, temperature and pressure should be higher than 30.978 °C and 1,070.0 psi, respectively.)
- Strong basicity (pH > 11) had detrimental effects on the Pd/TiO_{2-x} catalyst activity.

Accomplishment: Demonstrated the prototype CO_2-to-formate process to produce ammonium formate using pressurized CO_2 and H_2 gases





Temperature varies between 32-40 °C and stable at 35 °C, Stirring Speed (360 rpm), CO_2 Pressure (1252 psi),

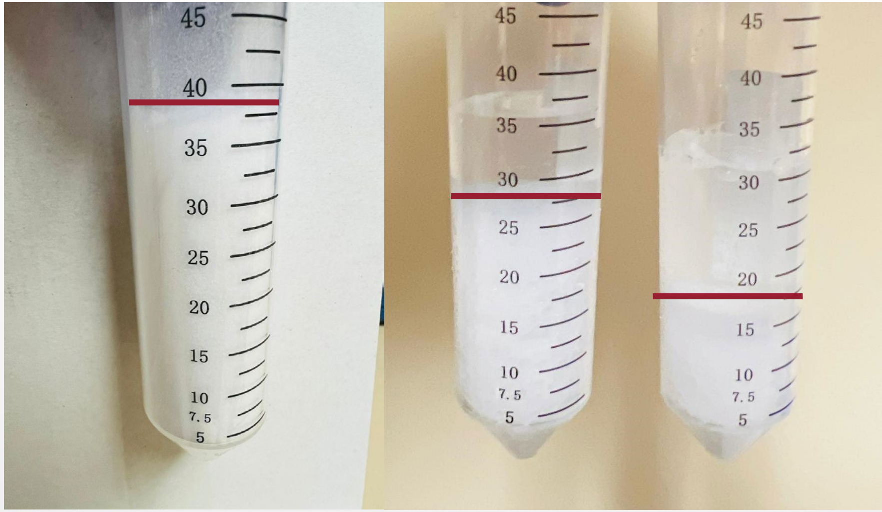
NH_3 (aq. 30 wt.%, ~7M, 25 mL) before and after 1 hour reaction with supercritical CO_2

- Supercritical CO_2 capture with aqueous ammonia (30 wt%) results in the solid ammonium bicarbonate precipitates. The rate of CO_2 capture with aqueous ammonia is much faster than the hydrogenation rate.
- We proposed a two-step process with decoupled CO_2 capture and conversion. Excess CO_2 was used to neutralize aqueous ammonia, without modifying the current experimental setup.

Accomplishment: Optimized operation conditions in the prototype CO_2-to-formate process

Table. Ammonium bicarbonate hydrogenation over Pd3/TiO_{2-x} at different conditions.

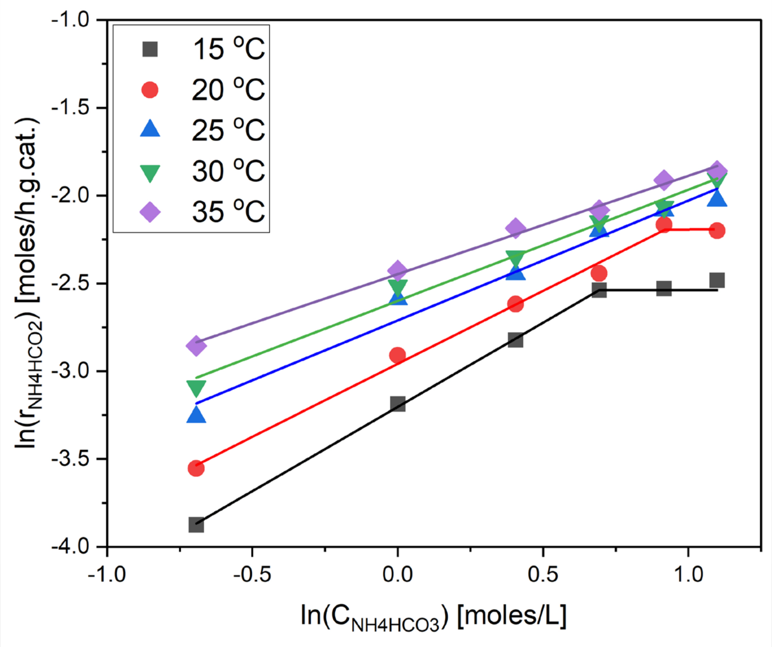
Weight (mg)	H_2 (psi)	t (h)	T (°C)	AB Conc. (M)	AF Conc. (M)
100	500	3	25	5	0.14
300	500	3	25	5	0.38
300	900	14	25	5	0.57
300	900	24	25	5	0.81
300	900	48	25	5	3.41
300	900	72	25	5	3.84
950	1000	30	35	7	4.70



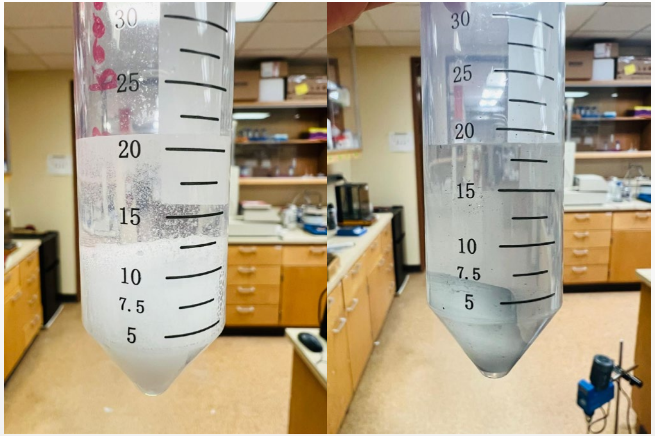
(Left to Right): 10M, 7M and 5M solution of ammonium bicarbonate in DI water.

- ❑ We demonstrated that the ammonium bicarbonate slurry solutions (up to 7M) were able to be hydrogenated to ammonium formate. With the extended hydrogenation time, we obtained up to 4.7M ammonium formate solutions.
- ❑ Due to the solubility limit, 10M ammonium bicarbonate solution appeared to be very dense slurry at room temperature, which was challenging to be hydrogenated with a solid catalyst.

Accomplishment: Optimized operation conditions in the prototype CO_2-to-formate process



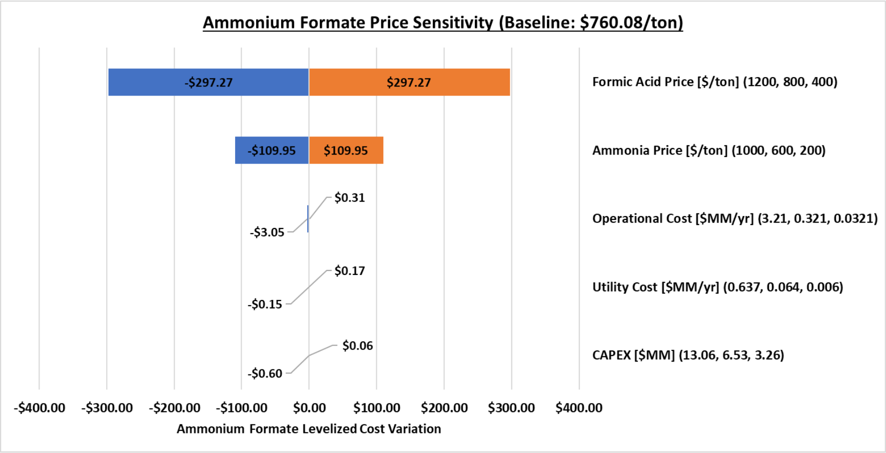
- ☐ We optimized the reaction conditions and investigated kinetics over various concentrations and temperatures.
- ☐ The activation energy of hydrogenation of ammonium bicarbonate: Ea = 27.91 kJ/mol.



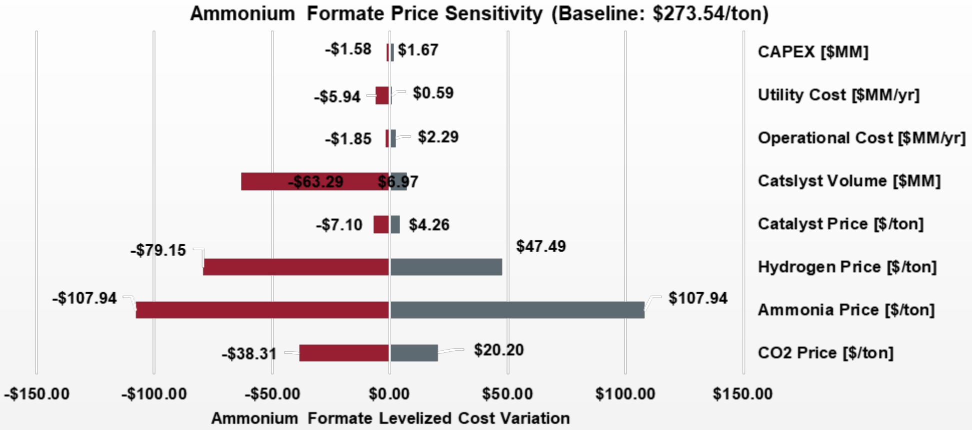
Samples before and after 72 hours of ammonium bicarbonate hydrogenation

- ☐ The 2-step process, i.e., CO_2 capture followed by ammonium bicarbonate hydrogenation, was feasible.
- ☐ The "one-pot" CO_2 capture and hydrogenation process may still be feasible if excess CO_2 could fully neutralize aqueous ammonia at the beginning.
- ☐ Over an extended reaction time, as more ammonium formates were produced, more ammonium bicarbonate precipitates were dissolved. After 72 hours, only a trace amount of solid ammonium bicarbonate could be observed.

Accomplishment: Demonstrated the prototype CO_2-to-formate process with a >30% cost reduction in the production of the ammonium formate



Conventional Ammonium Formate Synthesis Process



Proposed Ammonium Formate Synthesis Process

- ❑ Our proposed prototype CO_2 capture and hydrogenation process has an average **~64%** lower ammonium formate production cost ($273.54/ton) compared to the commercial ammonium formate production process ($760.08/ton).

Collaboration and Coordination

Organizations	Team Members	Roles
Pacific Northwest National Laboratory	Tom Autrey Katarzyna Grubel Mike Bowden Mark Engelhard	• Attend monthly project meetings • Validate catalyst performance results • Perform X-Ray Photoelectron Spectroscopy (XPS) analysis
Lawrence Livermore National Laboratory	Sneha A. Akhade Brandon Wood Thomas Ludwig Shyam Deo	• Attend monthly project meetings • Perform Density Functional Theory (DFT) calculations
8 Rivers Capital, LLC.	Phillip Cross Joe Weiner	• Attend monthly project meetings • Perform Techno-Economic Analysis (TEA)

Proposed Future Work

- ☐ 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 optimized the synthesis methods and prepared over 50 grams of the best-performing Pd on TiO2 catalysts with tunable oxygen vacancies. These catalysts exhibit high activity in the hydrogenation of ammonium bicarbonate. Moreover, we have demonstrated the catalyst's excellent long-term stability through 25 successive runs without any loss of activity.
- We have developed and built a prototype CO2-to-formate process that integrates CO2 capture and hydrogenation with aqueous ammonia solutions. We have optimized the operating conditions to produce a highly concentrated ammonium formate solution.
- Our techno-economic analysis suggests that the designed large-scale CO2-to-formate process, based on our prototype CO2 capture and hydrogenation process, has an average of approximately 64% lower production cost for ammonium formate ($273.54/ton) compared to the commercial production process ($760.08/ton).