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

Project ID: ST217

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Overview

Timeline

- Project start date: Feb. 12, 2020
- Project end date: Jan. 31, 2023*

*Project continuation and direction determined annually by DOE

Barriers

- The cost of hydrogen storage is too high
- Energy efficiency is a challenge for all hydrogen storage approaches.
- Durability of hydrogen storage systems is inadequate.

Budget

- Funding received in FY20

-- $339,972 (including $53,939 to partners)

Partners

- Navid Rafati, Damian Beauchamp, 8 Rivers Capital
- Katarzyna Grubel, Kriston Brooks, Pacific Northwest National Laboratory

Relevance

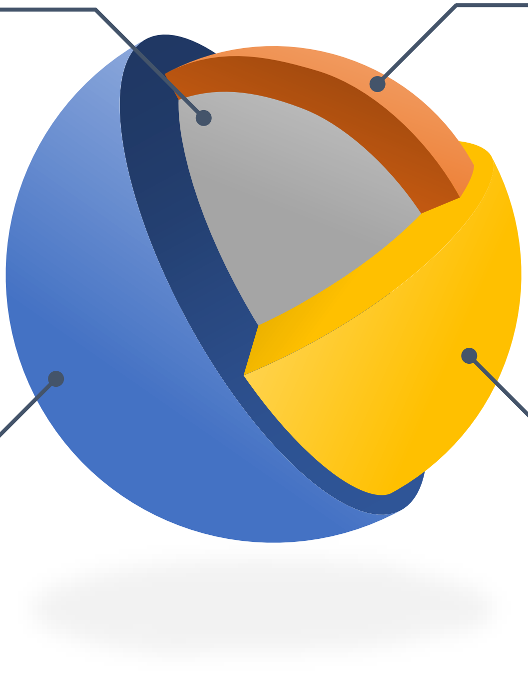
Objectives: build a prototype ammonium formate-based hydrogen uptake and release system and evaluate its techno-economic potential for commercialization.

- Collect the baseline performance data on the laboratory scale and develop the next-generation hydrogenation/dehydrogenation catalyst.
- Design, build and optimize a prototype CO_2-to-formate process to reduce the production cost of the formate hydrogen carrier.
- Design, build and optimize a prototype formate-to-power process and perform detailed technoeconomic analysis (TEA) and life cycle analysis (LCA) for validating the final project objectives.

Barriers from 2015 DOE target	Our technical target
The cost of hydrogen storage is too high	Pd loading <5% (commercial Pd loading); Pd dispersion >50%
Energy efficiency is a challenge for all hydrogen storage approaches.	TOF >1000 h^{-1}
Durability of hydrogen storage systems is inadequate.	>10 redox cycles operations

Approaches

FY20: Collect the baseline performance data on the laboratory scale and develop the next-generation catalyst



Step 1 (Q1)

Collect all the base line kinetic data of hydrogenation / dehydrogenation in 50 mL Parr reactor (including the activity and stability).

Step 2 (Q2-Q3)

Evaluate the performance of the **next-generation catalysts** and compare with **the commercial Pd/C** catalyst.

Step 3 (Q2-Q3)

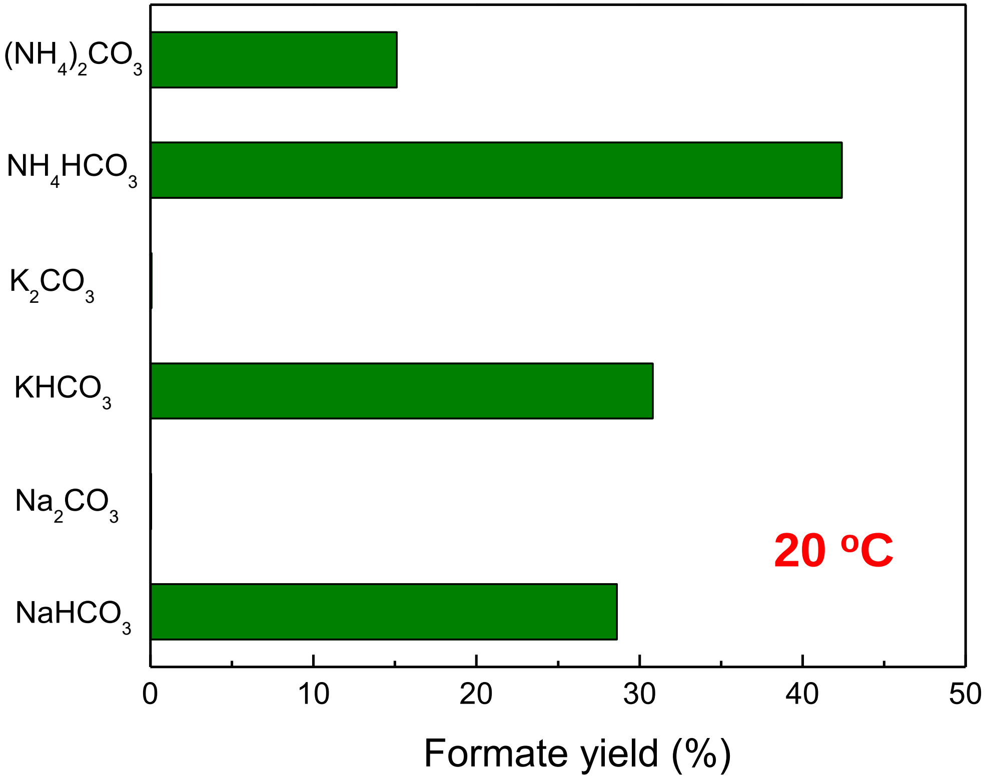
Synthesize and optimize the Pd-M bimetallic catalysts on nitrogen doped carbon supports.

Step 4 (Q2-Q4)

Perform the **characterization** of the next-generation catalysts and compare with the commercial Pd/C catalyst

Accomplishment

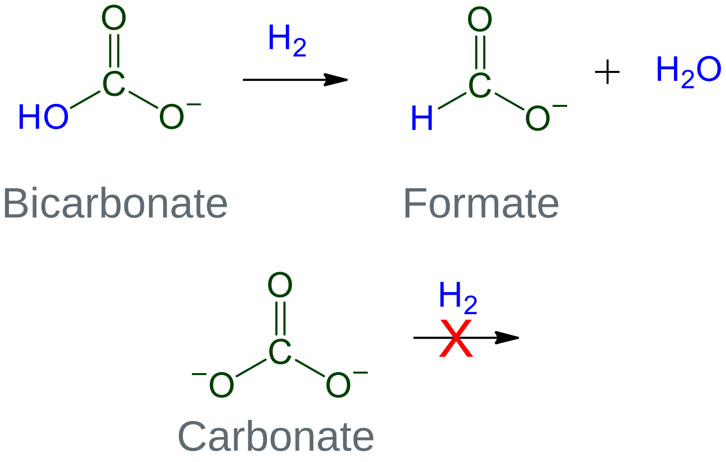
Hydrogenation process



Reaction conditions: 20 ml distilled H_2O, 0.02 mole reagent salts, 400 psi initial H_2 pressure , 0.1 g Pd/C catalyst (Pd loading is 5 wt %), 20 °C, 1 hour.

Catalytic hydrogenation kinetics:

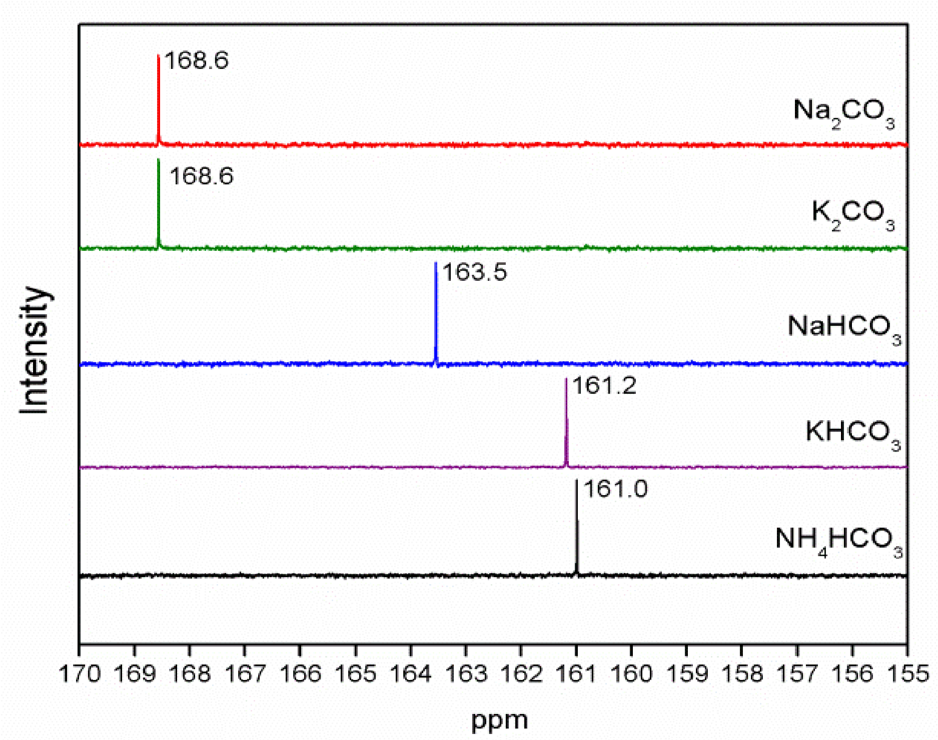
$NH_4HCO_3 > KHCO_3 > NaHCO_3 >$
$(NH_4)_2CO_3 >> K_2CO_3$ and Na_2CO_3



H_2 storage materials: NH_4HCO_3 vs $KHCO_3$ or $NaHCO_3$

Accomplishment

Hydrogenation process



^{13}C NMR spectra of Na_2CO_3, K_2CO_3, $NaHCO_3$, $KHCO_3$ and NH_4HCO_3 in H_2O. (Concentration is 1M.)

$$HCO_3^- \longleftrightarrow CO_3^{2-} + H^+$$

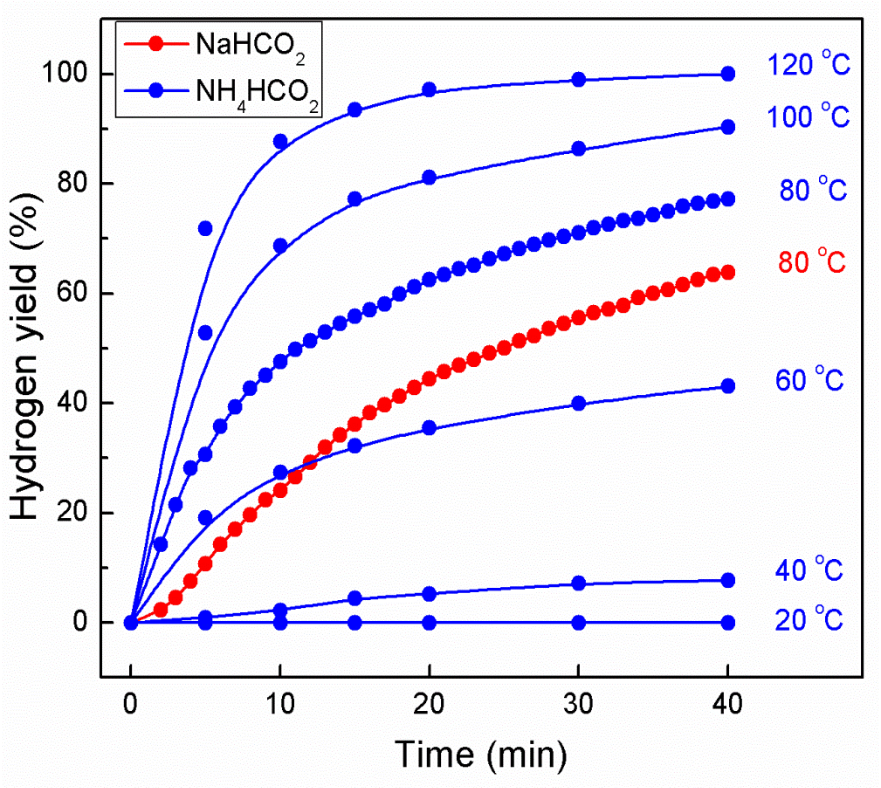
The peaks from 155 ppm to 170 ppm in ^{13}C NMR spectra were assigned to the **bicarbonate/carbonate ion pair** with fast proton exchange.

The concentrations of bicarbonate ions are in the order of: $NaHCO_3$ (**0.61M**) < $KHCO_3$ (**0.89M**) < NH_4HCO_3 (**0.92M**).

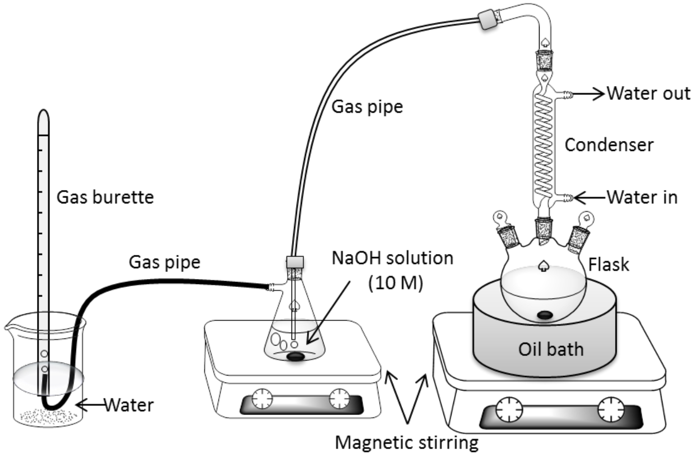
NH_4HCO_3 has the highest concentration of HCO_3^-, which is linked to the highest formate yield of hydrogenation reaction.

Accomplishment

Catalytic dehydrogenation of $HCOONH_4$ and HCOONa



Reaction conditions: 20 ml distilled H_2O, 0.02 mol formate, 0.1 g Pd/C catalyst (5 wt %), 1 atm initial N_2 pressure.

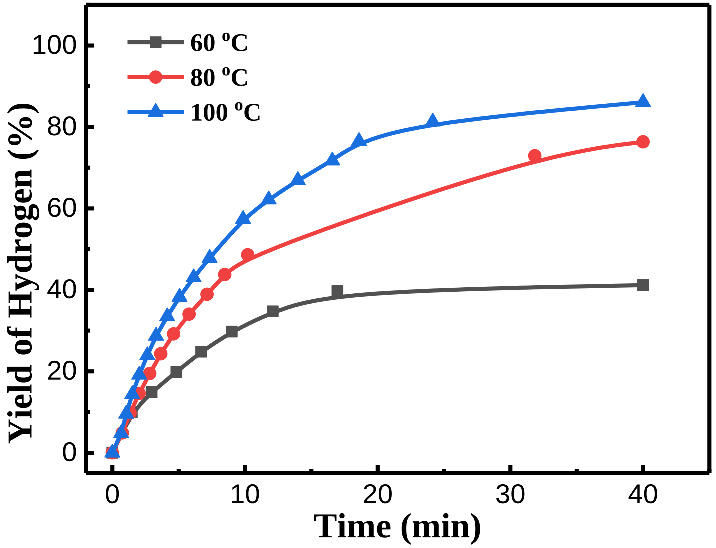


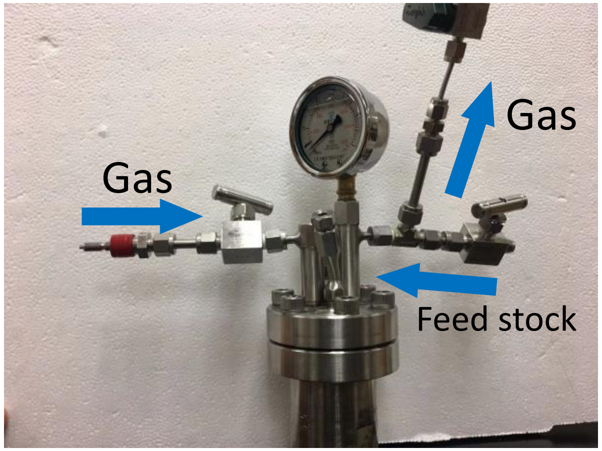
The schematic of formate dehydrogenation reaction system

- Ammonium formate was readily dehydrogenated over the commercial Pd/AC catalyst at T > 80°C
- Dehydrogenation of sodium formate is slower than that of ammonium formate

Accomplishment

Dehydrogenation of $HCOONH_4$ in the Parr reactor



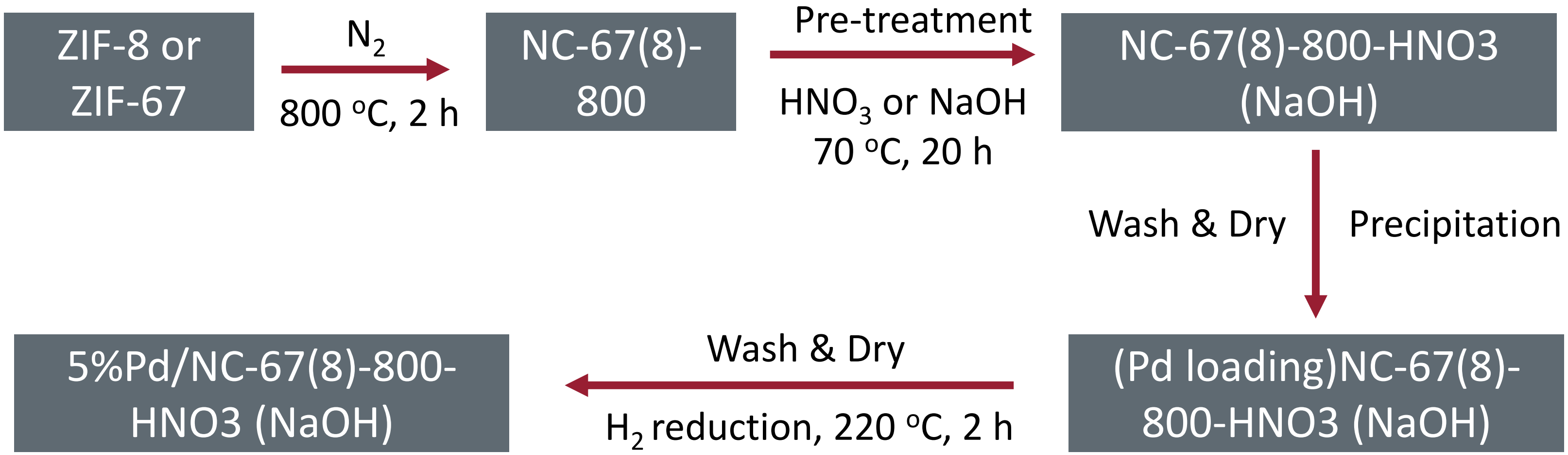


Temperature (°C)	Yield of H_2 (%)	
	50 mL Parr reactor	100 mL glass reactor
60	40.5	41.5
80	77.0	78.0
100	87.0	90.0

The dehydrogenation of ammonium formate in both 50-mL Parr reactor and 100-mL glass reactor achieved comparable H_2 yields.

Accomplishment

Synthesis of the next-generation Pd on nitrogen doped carbon catalysts



ZIF-8 or ZIF-67

N_2, 800 °C, 2 h

NC-67(8)-800

Pre-treatment, HNO_3 or NaOH, 70 °C, 20 h

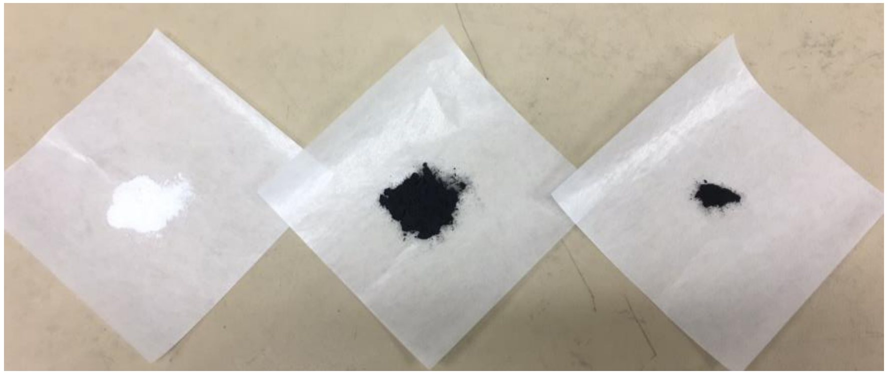
NC-67(8)-800-HNO3 (NaOH)

Precipitation, Wash & Dry

(Pd loading)NC-67(8)-800-HNO3 (NaOH)

Wash & Dry, H_2 reduction, 220 °C, 2 h

5%Pd/NC-67(8)-800-HNO3 (NaOH)



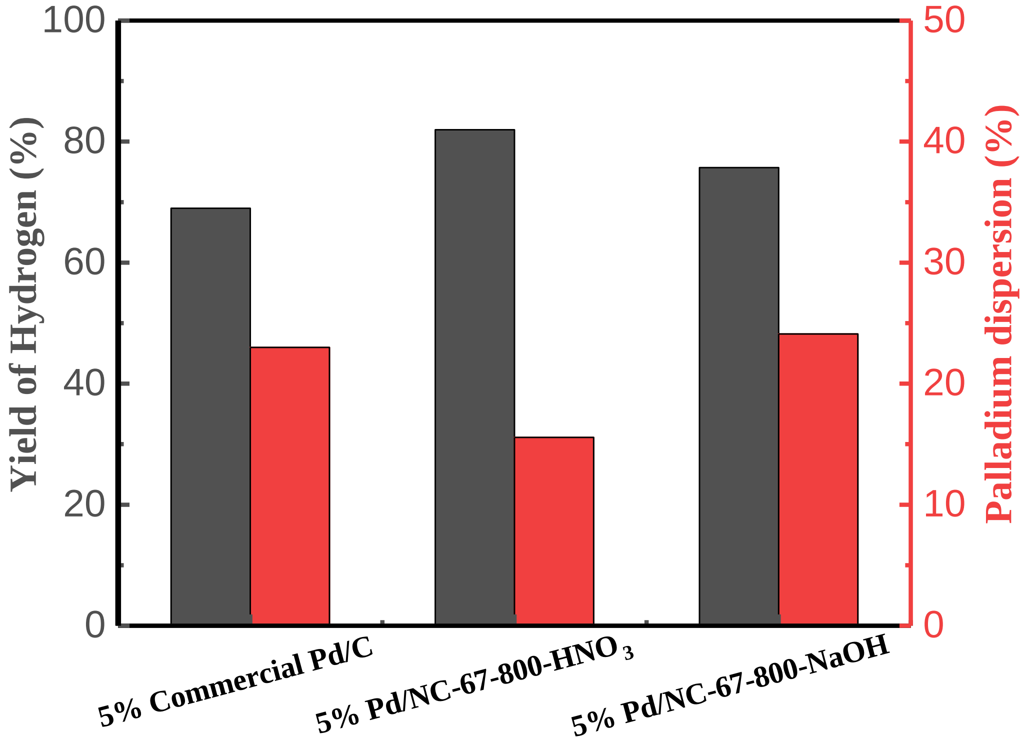
ZIF-8

NC-8-800-HNO_3

5%Pd/NC-8-800-HNO_3

Accomplishment

Development of the next-generation catalyst



* NC-67-800: nitrogen doped carbon support derived from ZIF-67 and calcinated at 800 °C;

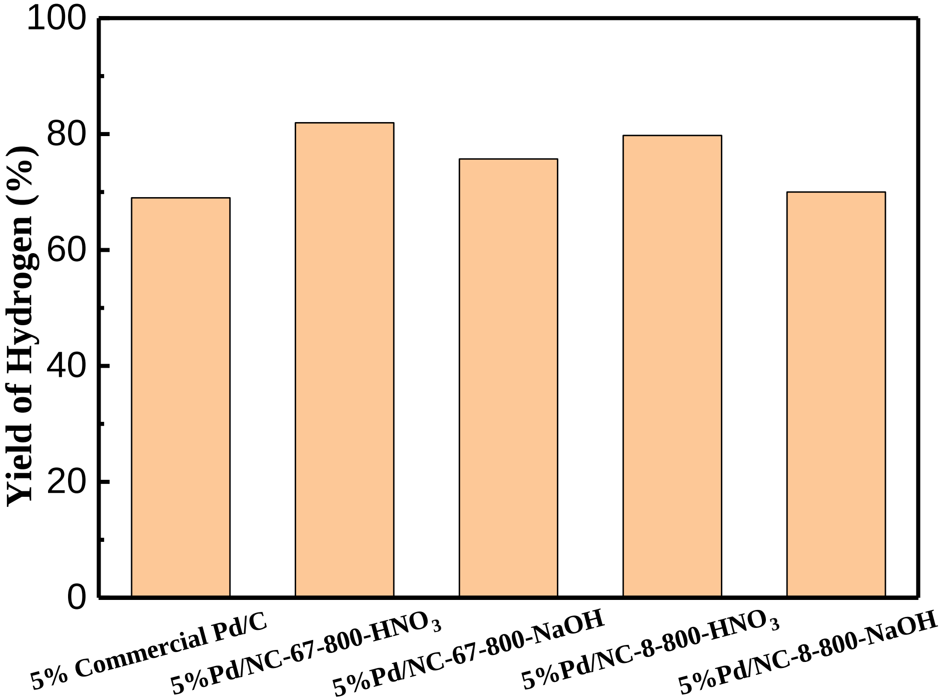
* NaOH (HNO_3): pre-treatment by NaOH (HNO_3) solution.

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

The next-generation Pd catalysts displayed the enhanced performance compared to the commercial Pd/C catalyst

Accomplishment

Developed the acid or base pre-treatment procedures for functionalization of carbon support

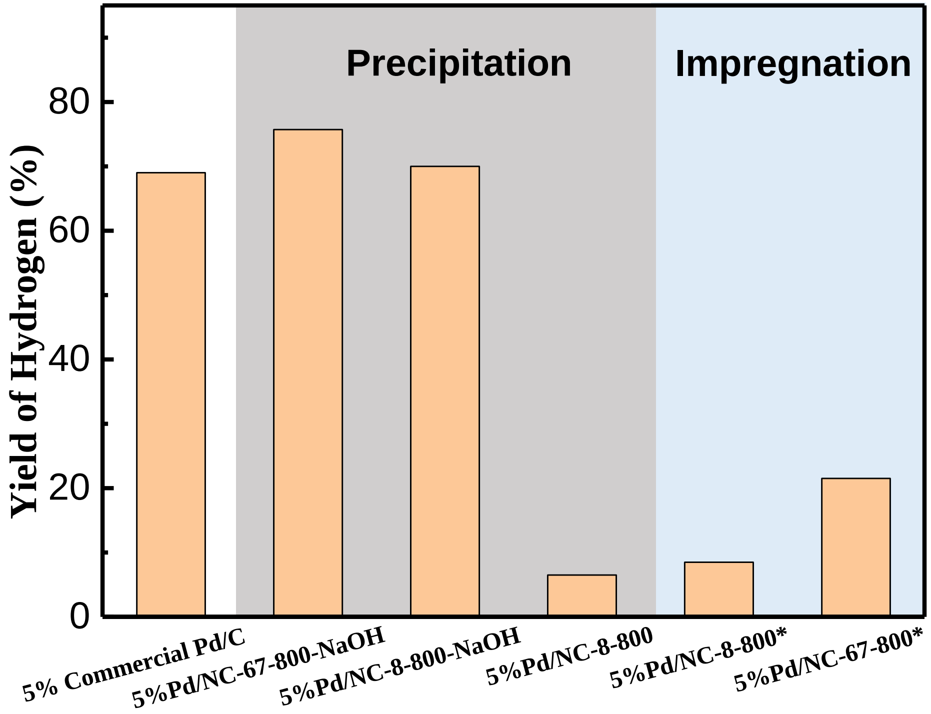


Catalyst	Yield of Hydrogen (%)	Dispersion (%)
Commercial Pd/C	69.0	23.0
5% Pd/NC-67-800-HNO_3*	82.0	15.6
5% Pd/NC-67-800-NaOH*	75.7	24.1

The HNO_3 pre-treatment of the carbon support enhanced the catalyst activity, while the NaOH pre-treatment increased the Pd dispersion

Accomplishment

Developed two synthesis methods to prepare the Pd on nitrogen doped carbon catalysts



*No “NaOH (HNO3)” in the catalyst name suggests no pre-treatment

The surface functionalization of carbon support improves the performance of the as-synthesized Pd catalysts

Accomplishment

- ***Built a continuous 450 mL CSTR reactor. The operation pressure is up to 1500 psi***

Response to previous year's review

- This project was not reviewed last year.

Collaborations

- Pacific Northwest National Laboratory
  - Katarzyna Grubel, Kriston Brooks
- 8 Rivers Capital
  - Navid Rafati, Damian Beauchamp
- Sandia National Laboratory
  - Jonathan Snider, Vitalie Stavila

Remaining Barriers and Challenges

Challenges of developing the next-generation catalysts

- Characterizations are insufficient to understand the physicochemical properties of the next-generation catalysts.
- The catalytic mechanisms during hydrogenation & dehydrogenation over the next-generation catalysts are not clearly understood.
- The durability and reliability of the next-generation catalysts need further assessment.
- The cost-effectiveness of the large-scale synthesis of the next-generation catalysts has not been demonstrated.

Proposed future work

Milestone	Description	Completed (%)
1	Collect the baseline performance data at the laboratory scale	50
2	Synthesize and characterize a variety of the Pd@N-doped carbon catalysts with various metal loadings in the range of 0.5 wt% to 5 wt%	20
	The TOF of both hydrogenation and dehydrogenation reactions (>1,000 h^{-1}), the catalyst stability (> 10 times cycle of both hydrogenation and dehydrogenation), and the Pd metal loading amount (< 5 wt%)	10

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

Tech Transfer Activities

- An international patent application entitled “hydrogen storage compositions, methods, and uses thereof” was filed on July 19, 2019. The application number is PCT/US2019/042705. This patent will be the underlying intellectual property for this funded project.

Summary

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

Relevance:

- Collect performance data of hydrogenation and dehydrogenation reactions on both commercial Pd/C catalyst and next-generation catalysts

Approaches:

- Use MOF (ZIF) as precursor to synthesize N-doped carbon supports
- Develop surface functionalization methods for the pretreatment of the catalyst support to improve the metal dispersion and to reduce the Pd metal loading
- Develop bimetallic catalysts to create synergistic effects, enhance the catalyst performance, and reduce the Pd metal loading.

Accomplishment:

- Collected the baseline performance data of ammonium formate dehydrogenation over the commercial Pd/C catalyst using a 50-mL Parr reactor.
- Synthesized the nitrogen doped carbon supported Pd catalysts and demonstrated the next-generation catalysts have comparable or better performance compared to the commercial Pd/C catalyst.