Pacific Northwest
NATIONAL LABORATORY

PNNL-36217

Methane Pyrolysis for CO2-free H2 and Carbon Nanomaterials (CRADA 576)

June 2024

Robert Dagle
Juan Lopez Ruiz
Nickolas Riedel
Keerti Kappagantula
Dalong Zhang
Carlos Fernandez

U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062
www.osti.gov
ph: (865) 576-8401
fox: (865) 576-5728
email: reports@osti.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312 ph: (800) 553-NTIS (6847)
or (703) 605-6000
email: info@ntis.gov
Online ordering: http://www.ntis.gov

PNNL-36217

Methane Pyrolysis for CO2-free H2 and Carbon Nanomaterials (CRADA 576)

June 2024

Robert Dagle
Juan Lopez Ruiz
Nickolas Riedel
Keerti Kappagantula
Dalong Zhang
Carlos Fernandez

Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99354

Cooperative Research and Development Agreement (CRADA) Final Report

Report Date: June 2024

In accordance with Requirements set forth in the terms of the CRADA, this document is the CRADA Final Report, including a list of Subject Inventions, to be provided to PNNL Information Release who will forward to the DOE Office of Scientific and Technical Information as part of the commitment to the public to demonstrate results of federally funded research. **PNNL acknowledges that the CRADA parties have been involved in the preparation of the report or reviewed the report.**

Parties to the Agreement:

Battelle

Sothern California Gas Company (SoCalGas)

C4-MCP

CRADA number: 576

CRADA Title: Methane Pyrolysis for CO_2-free H_2 and Carbon Nanomaterials

Responsible Technical Contact at DOE Lab(PNNL): Robert Dagle

Name and Email Address of POC at Partner Company(ies):

Southern California Gas Company: Flavio da Cruz (FDaCruz@socalgas.com)

C4-MCP**:** Jim McDermott (jim.mcdermott@rusheen.com)

Sponsoring DOE Program Office(s): N/A

Joint Work Statement Funding Table showing DOE funding commitment:

	Funding Amounts			
CRADA Parties	**DOE Funding ($K)**	**Funds-In ($K)**	***In-kind ($K)**	**Total ($K)**
Southern California Gas Company and C4-MCP	0	350	75	425
DOE Funding to PNNL	0	0	0	0
Total of all Contributions	0	350	75	425

Provide a list of publications, conference papers, or other public releases of results, developed under this CRADA:

No publication, conference papers, or other public releases were generated under this CRADA.

Provide a detailed list of all subject inventions, to include patent applications, copyrights, and trademarks:

No subject inventions were generated under this CRADA.

Executive Summary of CRADA Work

In this CRADA project we continued to develop the Pacific Northwest National Laboratory (PNNL) patent-pending Regenerable Catalytic Pyrolysis (ReCaP) process technology for producing CO_2-free hydrogen (H_2) from inexpensive and domestically-abundant natural gas (NG), while simultaneously reducing H_2's net production cost to $1.0/kg through the sale of valuable crystalline solid carbon co-product. Producing clean hydrogen at this price is a DOE Hydrogen Energy Earthshot goal. This effort builds on our prior catalyst and processing advances made thermocatalytic decomposition of methane (TCD) [1-4]. The additional scope performed here accelerated the commercial deployment of TCD for CO_2-free H_2 and valuable solid carbon nanotubes (CNT) co-product, by i) scaling up the production of CNT co-product using a fluidized bed reactor (25 g catalyst scale versus the 1 g catalyst scale demonstrated prior), ii) producing approximately 1 kg of CNT byproduct, produced via multiple cycles of TCD, carbon-catalyst separation, and catalyst re-synthesis, to enable the production of sufficient quantities of solid carbon so as to explore its market potential, iii) understanding the quality of the co-product CNTs, produced at larger scale, using advanced characterization, and iv) beginning to explore multiple promising high volume carbon product applications (e.g., aluminum and polymer composites, steel additive, and cement reinforcement applications). We are in discussions with Department of Energy and potential commercial partners to continue funding of this effort with the goal to facilitate eventual commercial deployment.

Summary of Research Results

This product contains Protected CRADA Information, which was produced on 1/12/24 under CRADA No. 576 and is not to be further disclosed for a period of five (5) years from the date it was produced except as expressly provided for in the CRADA.

Executive Summary

In this CRADA project we continued to develop the Pacific Northwest National Laboratory (PNNL) patent-pending Regenerable Catalytic Pyrolysis (ReCaP) process technology for producing CO_2-free hydrogen (H_2) from inexpensive and domestically-abundant natural gas (NG), while simultaneously reducing H_2's net production cost to $1.0/kg through the sale of valuable crystalline solid carbon co-product. Producing clean hydrogen at this price is a DOE Hydrogen Energy Earthshot goal. This effort builds on our prior catalyst and processing advances made thermocatalytic decomposition of methane (TCD) [1-4]. The additional scope performed here accelerated the commercial deployment of TCD for CO_2-free H_2 and valuable solid carbon nanotubes (CNT) co-product, by i) scaling up the production of CNT co-product using a fluidized bed reactor (25 g catalyst scale versus the 1 g catalyst scale demonstrated prior), ii) producing approximately 1 kg of CNT byproduct, produced via multiple cycles of TCD, carbon-catalyst separation, and catalyst re-synthesis, to enable the production of sufficient quantities of solid carbon so as to explore its market potential, iii) understanding the quality of the co-product CNTs, produced at larger scale, using advanced characterization, and iv) beginning to explore multiple promising high volume carbon product applications (e.g., aluminum and polymer composites, steel additive, and cement reinforcement applications). We are in discussions with Department of Energy and potential commercial partners to continue funding of this effort with the goal to facilitate eventual commercial deployment.

Summary

Summary of key accomplishments made on the project:

- A fluidized bed rector system was designed, fabricated, and tested for the methane pyrolysis reaction at the 25 g catalyst scale. Catalyst activity, selectivity, and stability was evaluated at different reactor temperatures, feed partial pressures, and weight hour space velocities.

- Using our previously developed Ni-based catalyst formulation (25 g) [5], a 50% methane single pass conversion was initially achieved under fluidized bed operation and continuously operated for 260 hours' time-on-stream when using pure methane feed and at 600^{o}C and atmospheric pressure. Over the course of the run a CNT carbon yield of19.7 $g_{carbon}/g_{catalyst}$ was achieved. Future work will involve continuous catalyst/ product removal, catalyst regeneration, and re-addition of regenerated catalyst to increase catalyst lifetime and overall yield to H_2 and CNT products.

- A total of approximately 1 kg CNT was produced over multiple campaigns of TCD, carbon-catalyst separation, and catalyst re-synthesis.

- Resulting characterization of the product solid carbon reveled it to be a multi-walled carbon nanotube (MWCNT) structure. Further it was shown how the characteristics of the MWCNT changed after performing multiple cycles of separation and resynthesis, and at various time-on-stream using advanced characterization techniques (e.g., Raman IR, HTEM).

- Produced CNT was used to begin to explore how multiple promising high volume carbon product applications could be produced.
- It was demonstrated how 1.0 wt.% CNT addition to steel significantly improved its hardness (100%) and strength (50%). By using conventional extrusion approaches, we believe the CNTs would lose their structure. However, by using a PNNL proprietary approach the crystallinity likely remained intact
- It was demonstrated how the addition of 5 wt.% CNT to aluminum composite improved its ultimate tensile strength by >13%.
- The addition of up to 10 wt.% CNT to polymer composite composed of high-density polyethylene and lignite particles was found to improve its flexural strength and modulus.
- The addition of 0.05% CNT was demonstrated to improve the flexural (50% higher) and tensile (22% higher) strength of a cement mixture. This preliminary finding suggests that ReCaP-CNTs could offer performance enhancement to binder cement for its potential application in concrete infrastructure, as has been reported in the literature when using conventional (expensive) CNTs.
- Techno-economic analysis (TEA) projects a $1.0/kg H_2 production cost, given current market price of natural gas feedstock and a minimum carbon selling price (MCSP) of $1.8 – 7.5/kg (pricing dependent on production scale).

Pacific Northwest National Laboratory

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99354
1-888-375-PNNL (7665)

www.pnnl.gov

References

[1] Hu, J.; Wang, I.-W.; Li, L.; Dagle, R. A.; Lopez-Ruiz, J. A.; Xu, M.; Davidson, S. Methods and Compositions for Production of CO2-free Hydrogen and Carbon Nanomaterials by Methane Decomposition. U.S. Patent Application 2022/0339609 A1, 2022.
[2] M. Xu, J.A. Lopez-Ruiz, L. Kovarik, M.E. Bowden, S.D. Davidson, R.S. Weber, I.W. Wang, J. Hu, R.A. Dagle, Structure sensitivity and its effect on methane turnover and carbon co-product selectivity in thermocatalytic decomposition of methane over supported Ni catalysts, Applied Catalysis A: General, 611 (2021) 117967.
[3] I.W. Wang, R.A. Dagle, T.S. Khan, J.A. Lopez-Ruiz, L. Kovarik, Y. Jiang, M. Xu, Y. Wang, C. Jiang, S.D. Davidson, P. Tavadze, L. Li, J. Hu, Catalytic decomposition of methane into hydrogen and high-value carbons: combined experimental and DFT computational study, Catalysis Science & Technology, 11 (2021) 4911-4921.
[4] R.S. Weber, M. Xu, J.A. Lopez-Ruiz, C. Jiang, J. Hu, R.A. Dagle, Toward Rational Design of Nickel Catalysts for Thermocatalytic Decomposition of Methane for Carbon Dioxide-Free Hydrogen and Value-Added Carbon Co-Product: A Review, ChemCatChem, n/a e202301629.
[5] M. Xu, J.A. Lopez-Ruiz, N.W. Riedel, R.S. Weber, M.E. Bowden, L. Kovarik, C. Jiang, J. Hu, R.A. Dagle, Promotional role of NiCu alloy in catalytic performance and carbon properties for CO2-free H2 production from thermocatalytic decomposition of methane, Catalysis Science & Technology, 13 (2023) 3231-3244.