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Investigation of a Novel Pyrolyzed PDMS/Ni Catalyst for Dry Reforming of Methane (DRM)

Miami University – Department of Chemical, Paper, and Biomedical Engineering

Undergraduate Student: Rachel Olp
Advisors: Dr. Catherine Almquist, Dr. Keith Hohn

MIAMI UNIVERSITY

INTRODUCTION & AIM

Purpose: Develop a catalyst that improves catalyst long-term stability for the DRM reaction

Background

Main reaction:

$$CH_4 + CO_2 \leftrightarrow \underbrace{2\,CO + 2\,H_2}_{\text{Syngas}} \quad (1)$$

Side reactions:

$$2\,CO \leftrightarrow C(s) + CO_2 \quad (2)$$
$$CH_4 \leftrightarrow C(s) + 2\,H_2 \quad (3)$$
$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad (4)$$
$$H_2 + CO \leftrightarrow H_2O + C(s) \quad (5)$$

Issue

Boudouard (2), methane decomposition (3), and other reactions contribute to coking and sintering of catalyst, causing rapid deactivation.

Hypothesis

Pyrolyzed nickel (Ni)-containing polydimethylsiloxane (PDMS) will result in a high surface area, thermally-stable and coke-resistant catalyst for the DRM reaction. Ni will experience stable dispersion into nano-sized particles on the resulting Si-O-C support.

Objectives

1) Investigate the effects of Ni on the physical and chemical characteristics of pyrolyzed polydimethylsiloxane (PDMS)
2) Determine the effect of Ni loading, reactant molar ratio, and reaction temperature on the performance of pyrolyzed Ni-containing PDMS in the DRM reaction.

Performance is defined in this study as:

a) Catalytic activity (TOF, % conversion of CH_4, H_2/CO ratio)
b) Degradation in activity (activity loss) over 11 hours of continuous runtime

Why Nickel?

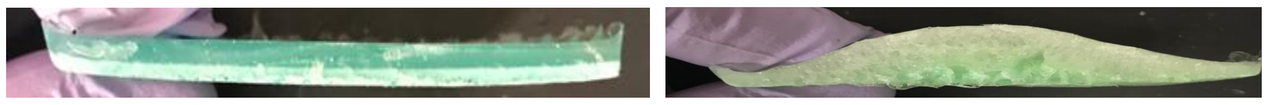
- Economical active metal [2,5]

Why pyrolyzed polydimethylsiloxane (PDMS)?

- Provides microporous and mesoporous support that provides stability to the active metal. [2,3]
- Smaller Ni particle size and higher dispersion, reported to result in catalyst stability and coke-resistance [1,2,4]
- Active metal stability prevents sintering of catalyst over reaction period. [4]

SYNTHESIS & CHARACTERIZATION

1. PDMS mixed with curing agent at recommended ratio
2. Hydrated Nickel acetate [$Ni(CH_3CO_2)_2 \cdot 4\,H_2O$] mixed in until evenly dispersed
3. Membrane cured for 2.5 hours in varying conditions

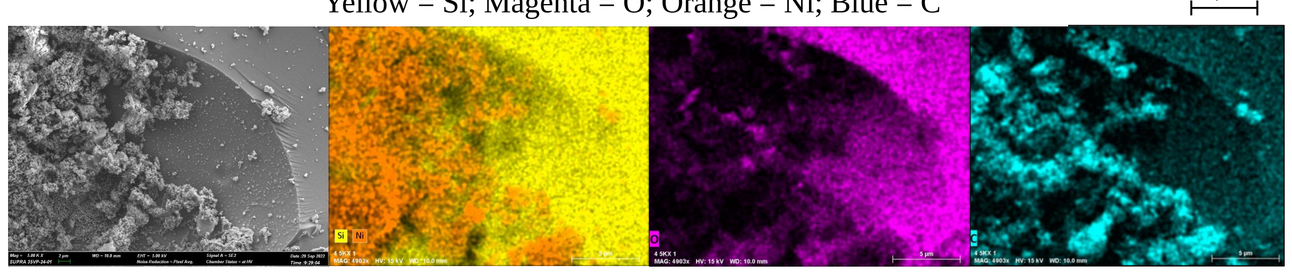


6 Ni-PDMS membrane, anaerobically vacuum cured 2 Ni-PDMS membranes, aerobically oven cured

4. 1-3mm pieces of membrane placed in ceramic boat loaded in metal tubing chamber
5. Chamber purged in Argon at 150ºC overnight, then pyrolyzed at 750 ºC for 2 hours, cooled
6. Pyrolyzed PDMS membrane crushed through sieve to produce particles < 0.23 mm diameter

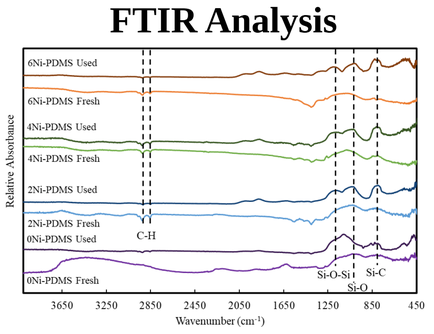
SEM Images of 4Ni-PDMS, 5000X Magnification.

Yellow = Si; Magenta = O; Orange = Ni; Blue = C



Catalyst ID	Nominal Initial mass Ni/Si ratio	TGA calculated[2] Ni/Total mass ratio	EDS mass Ni/Si ratio
0Ni-PDMS	0	0	0
2Ni-PDMS	0.054	0.046	0.147
4Ni-PDMS	0.110	0.143	0.202
6Ni-PDMS[1]	0.296	0.454	0.321

FTIR Analysis



Catalyst ID	Surface Area (m^2/g)	Pore (Micropore) Volume (cm^3/g)	Average Pore (Micropore) Width (Å)	Ni Crystal Size[3] (nm)
0Ni-PDMS	520	0.222 (0.198)	17.2 (16.2)	0
2Ni-PDMS	409	0.195 (0.153)	19.3 (16.6)	33.4
4Ni-PDMS	337	0.168 (0.123)	20.2 (16.6)	36.2
6Ni-PDMS[1]	417	0.231 (0.172)	22.8 (17.8)	30.6

[1] This catalyst settle before curing, leading to a non-homogenous distribution of the Ni in the PDMS prior to pyrolysis. Samples may not have been representative of overall catalyst composition.
[2] The calculated Ni/Total mass ratio was based upon the assumption of no loss of Ni during pyrolysis.
[3] Calculated using the Scherrer Equation and XRD profiles.

RESULTS & DISCUSSION

Catalyst ID [Ref]	CH_4 Conversion	Activity loss	CH_4 TOF[4] (sec^{-1})
2Ni-PDMS	13%	48.6%	0.148
4Ni-PDMS	34%	18.2%	0.315
6Ni-PDMS	46%	9.7%	0.252
Ni-SiO_2 [2]	58%	5%	33.4
Ni/SBA-15-EG [3]	32%	13.3%	0.0635
Ni/SBA-15-H_2O [3]	20%	18.7%	0.0579
NiAl-C [5]	74%	1%	1.48

[4] TOF: Turnover Frequency

All reactions in this study are run with total flow of 60 ccpm, with results measured by gas chromatography.
Parameters are 750ºC, 1:1:1 CH_4:CO_2:N_2 unless otherwise stated

FUTURE WORK / REFERENCES

[1] D. Baudouin, U. Rodemerck, F. Krumeich, A. Mallmann, K.C. Szeto, H. Ménard, L. Veyre, J.-P. Candy, P.B. Webb, C. Thieuleux, C. Copéret, C. Journal of Catal. 297 (2013) 27–34.
[2] J. Zhang, Fanxing Li. Appl. Catal. B 176-177 (2015) 513–521.
[3] T. Xie, L. Shi, J. Zhang, D. Zhang, Chem. Commun. 50 (2014) 7250–7253.
[4] X. Zhang, Q. Zhang, N. Tsubaki, Y. Tan, Y. Han. Fuel 147 (2015) 243–252
[5] X. Zhu, P. Huo, D. Cheng, C. Liu. Appl. Catal. B 81, 1-2 (2008) 132–140

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CONCLUSION

- Catalysts demonstrated comparable TOF, CH_4 conversion, and activity loss to some literature
- The pyrolyzed PDMS support was largely microporous
- Nickel particles were nano-sized but did not disperse evenly across PDMS support surface area
- The catalysts are non-homogenous in composition and structure.
- 6% Ni loading of PDMS support displays the highest % CH_4 conversion and lowest activity loss in DRM reaction studied in this research
- A reaction temperature of 750°C demonstrated the highest % CH_4 conversion of all reaction temperatures studied in this research
- A molar ratio of 2:1 CH_4:CO_2 demonstrated a H_2/CO ratio closest to 1 of all reactant ratios studied in this research