Early Transition Metal Carbides and Nitrides for Ammonia Synthesis

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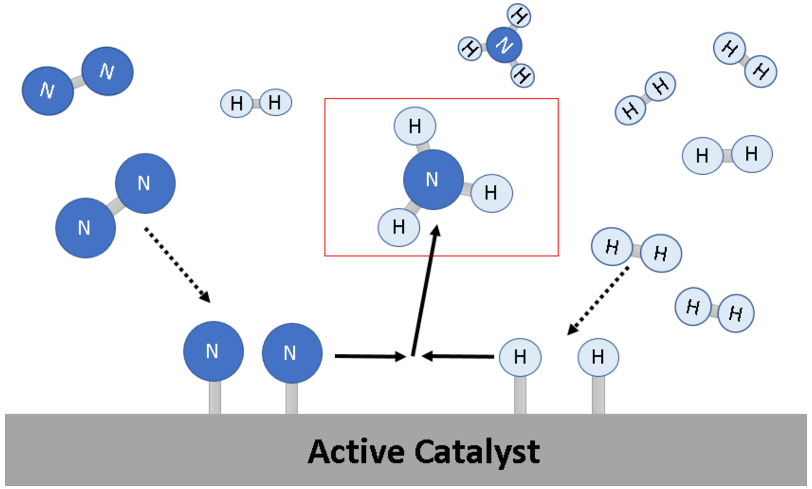
UNIVERSITY OF MICHIGAN

Thermochemical Process for Ammonia Synthesis

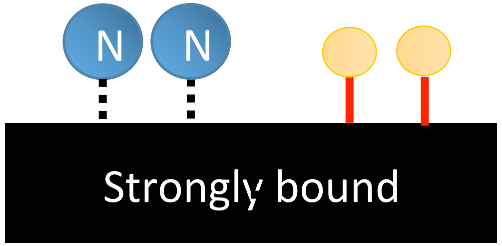
Major challenges [1]

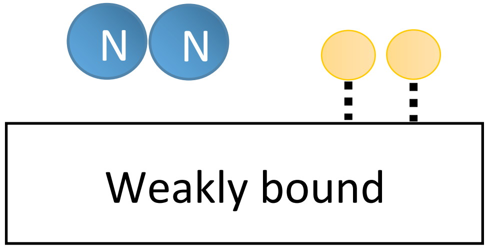
- Inefficient



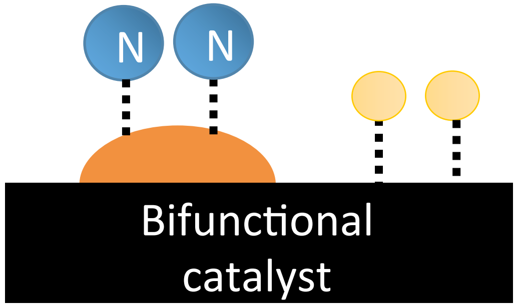
Opportunity
Alternative catalysts

Approach
Bifunctional catalyst [3]





N ≡ N	941 kJ/mol
H—H	432 kJ/mol
N—H	391 kJ/mol

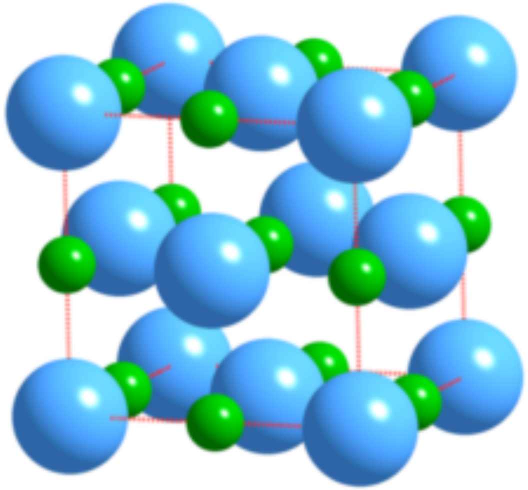


[1] Nørskov, J.; Contacts, B.; Miranda, R.; Fitzsimmons, T.; Stack, R.; Singh, A.; Rohr, B.; University, S.; Goldstein, J. 2016.
[2] T. L. Cottrell, *The Strengths of Chemical Bonds, 2d ed.* 1958.
[3] Schweitzer, N. M.; Schaidle, J. A.; Ezekoye, O. K.; Pan, X.; Linic, S.; Thompson, L. T. *J. Am. Chem. Soc* 2011, *133*, 2378–2381.

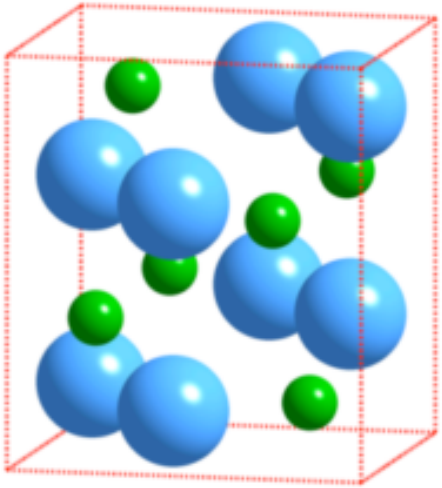
Carbides and Nitrides for Catalysis

Applications in heterogeneous catalysis [1]:

- Hydrogenation
- Isomerization
- Hydrogenolysis
- Methanation



FCC: α-Mo_2C_{1-x}, γ-Mo_2N



HCP: β-Mo_2C

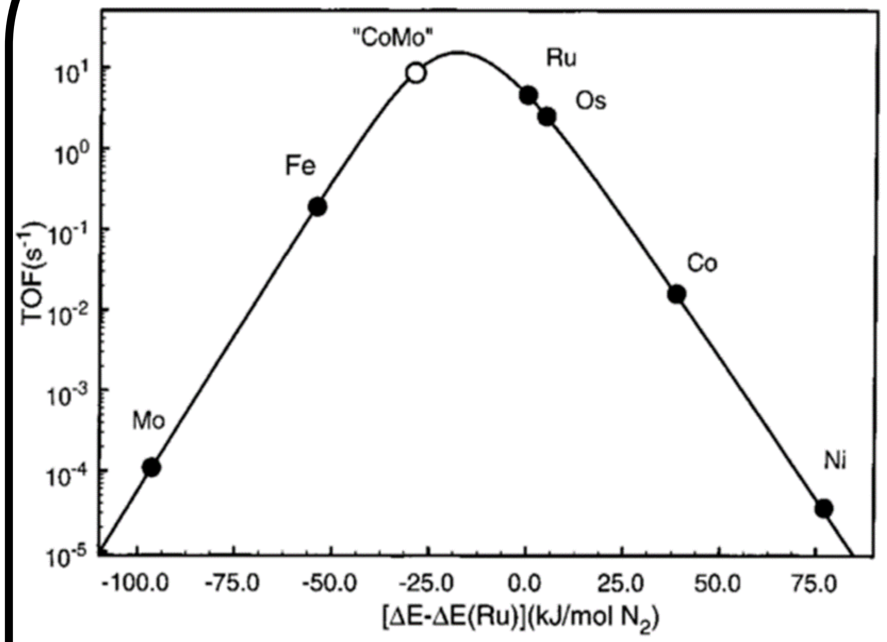
Material properties [1,2]:

- Similar to ceramics in terms of strength and hardness
- Similar to precious metals for electronic properties
- High surface area

[1] Oyama, S. T. *Catal. Today* **1992**, *15* (2), 179–200.
[2] Oyama, S. T. et al. *The Chemistry of Transition Metal Carbides and Nitrides* 1996.

Ternary Nitrides for Ammonia Synthesis

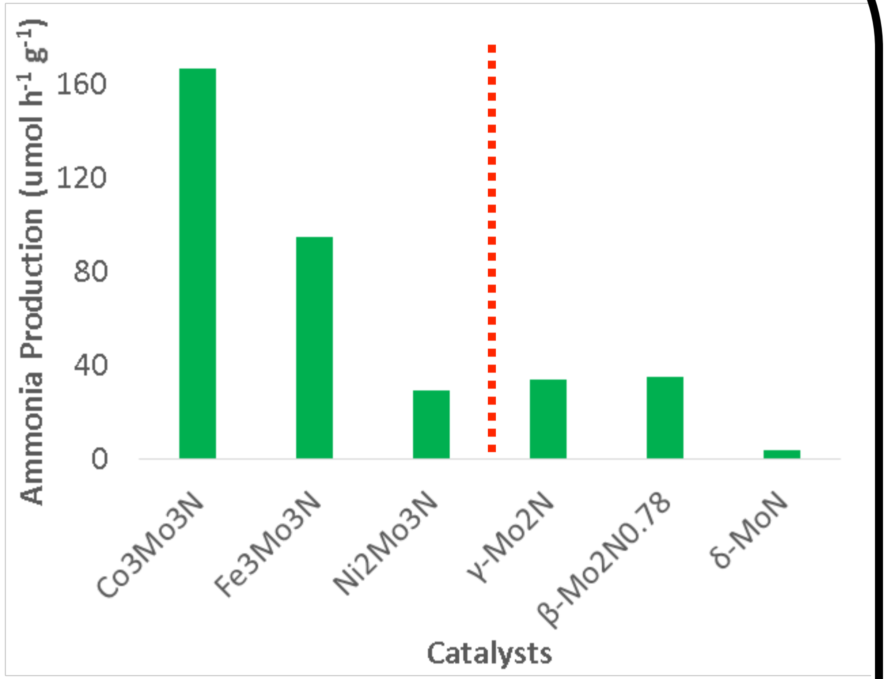
Volcano Plot of for Ammonia Synthesis



Model conditions:
400 °C, 50 bar, 3:1 balance of H_2:N_2

Co-Mo catalyst at optimum ammonia synthesis adsorption energy [1]

Ternary Mo_2N Comparison



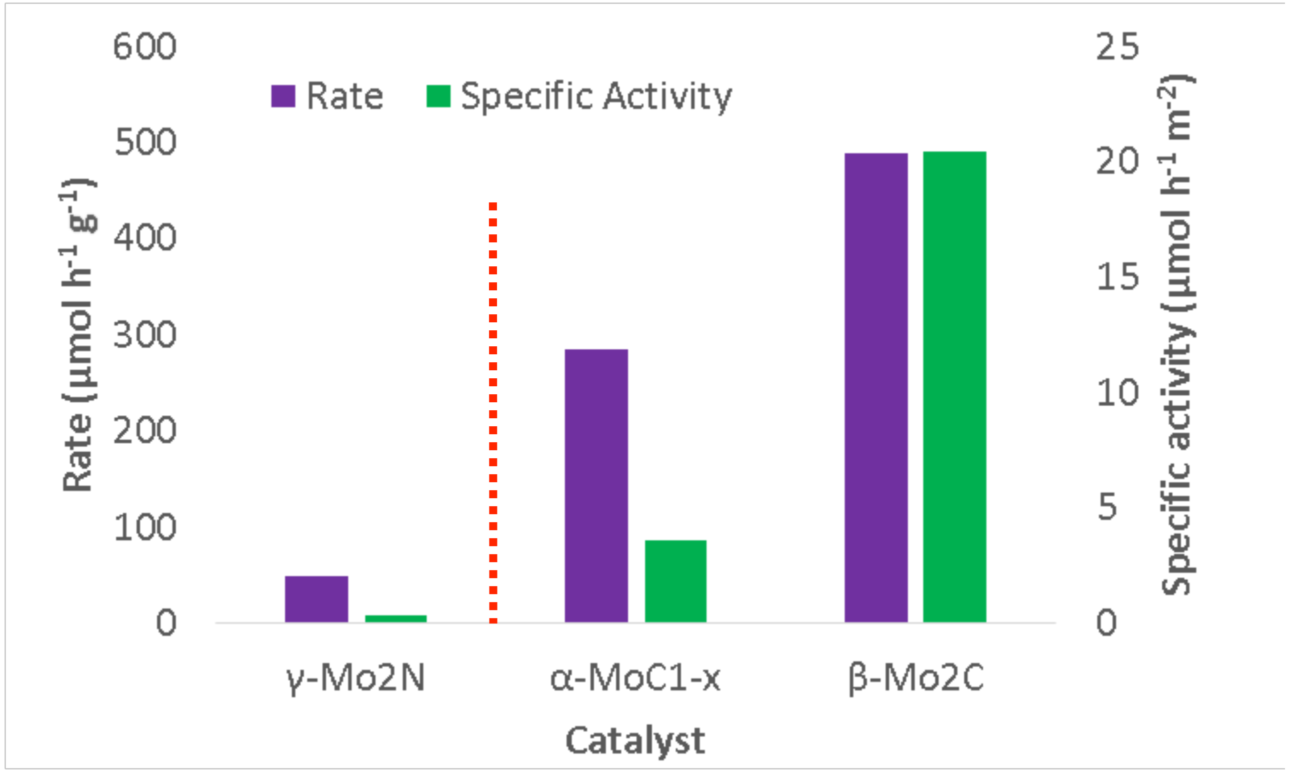
Experimental conditions:
400 °C, 1 bar, 3:1 balance of H_2:N_2

Co_3Mo_3N catalyst resulted in highest ammonia production levels [2]

[1] Jacobsen et al, *J. Am. Chem. Soc.* **2001**, *123* (34), 8404–8405.
[2] Mckay, D. et al, *J. Solid State Chem.* **2008**, *181* (2), 325–333.

Carbides for Ammonia Synthesis

Comparing Mo_2C and Mo_2N



Both phases of the Mo_2C resulted in higher production rates than the Mo_2N [1]

Gap in body of knowledge: ternary Mo_2C-based material for ammonia synthesis

[1] Kojima, R.; Aika, K. I. *Appl. Catal. A Gen.* **2001**, *219* (1–2), 141–147.

Hypothesis

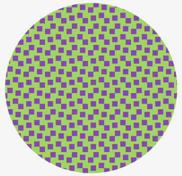
Bifunctional catalyst with metal domains for N-N activation and support domains for nitrogen hydrogenation will be highly active for low-temperature ammonia synthesis.

Synthesis technique for high surface area carbides and nitrides

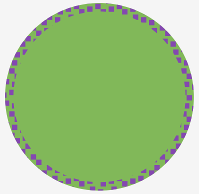
Catalyst	Kojima SA [1]	Thompson
Mo_2C	32	91
Co_3Mo_3N	52	-
Co/Mo_2N	-	132

Metal-deposited Mo_2C and Mo_2N

Ternary [2]



Metal-loading



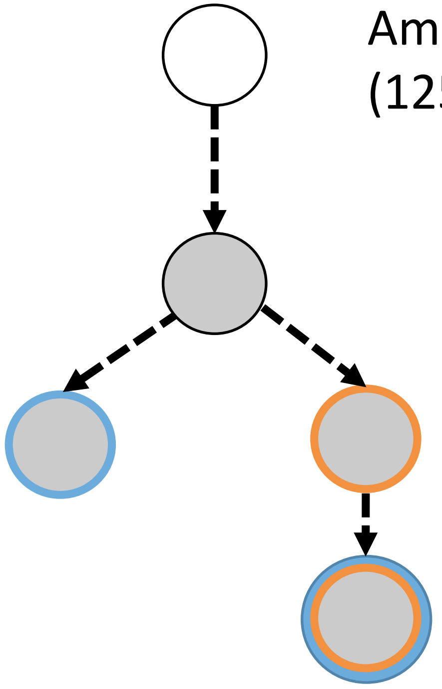
Bifunctional catalytic properties

Different metals on the support would allow us to design the surface of the catalyst to optimize ammonia production

[1] Kojima, R.; Aika, K. I. *Appl. Catal. A Gen.* **2001**, *215*, 149–160.
[2] Kojima, R.; Aika, K. I. *Appl. Catal. A Gen.* **2001**, *218* (1–2), 121–128.

Experimental Methods

Synthesis and Metal Loading

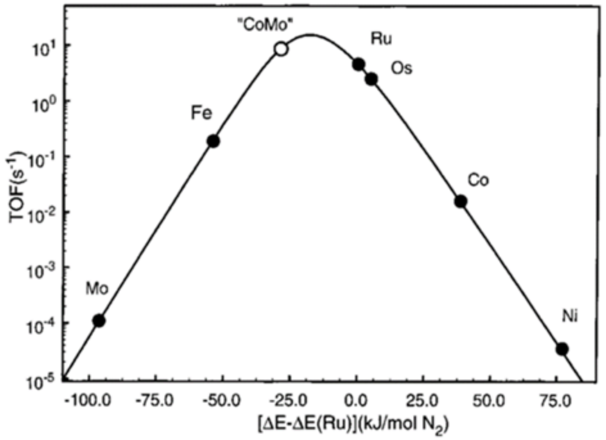


Ammonium paramolybdate (125 – 250 µm)

Temperature programmed reaction

0.5 ML Metal deposition

Passivate with 1% O_2/He flow, > 5 hours



Selected metals:
Fe, Ru, Co

Characterization

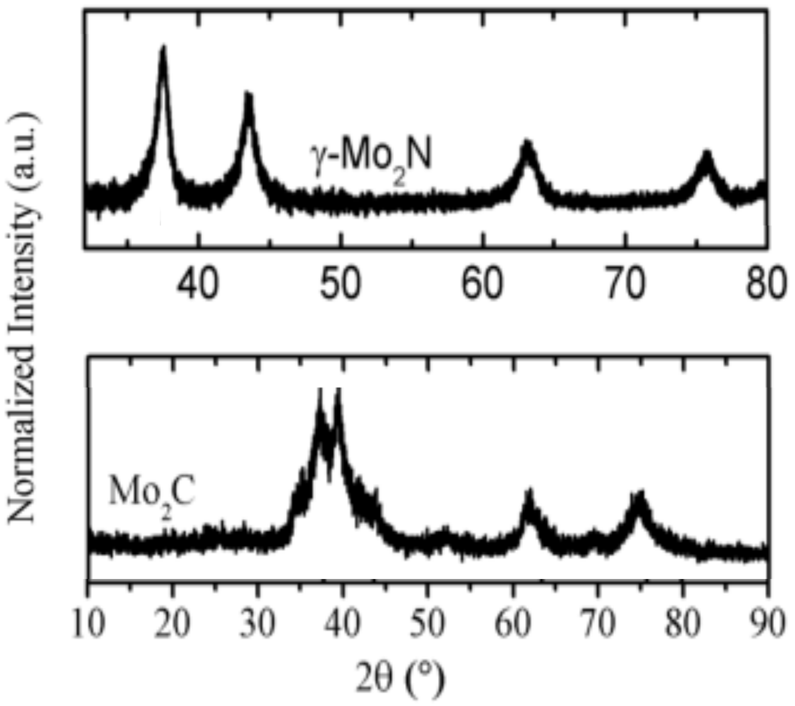
- X-ray diffraction (XRD): crystal structure
- N_2 physisorption: BET surface area calculation

Performance

- Temperature programmed reaction: NH_3 production rate
- Reaction conditions: ramp from 40 – 800 °C under 25% N_2/H_2
- Mass spectrometer

Material Characterization

X-ray Diffraction



- Synthesize phase pure bulk material
- Loading the metal results in high dispersion on the surface

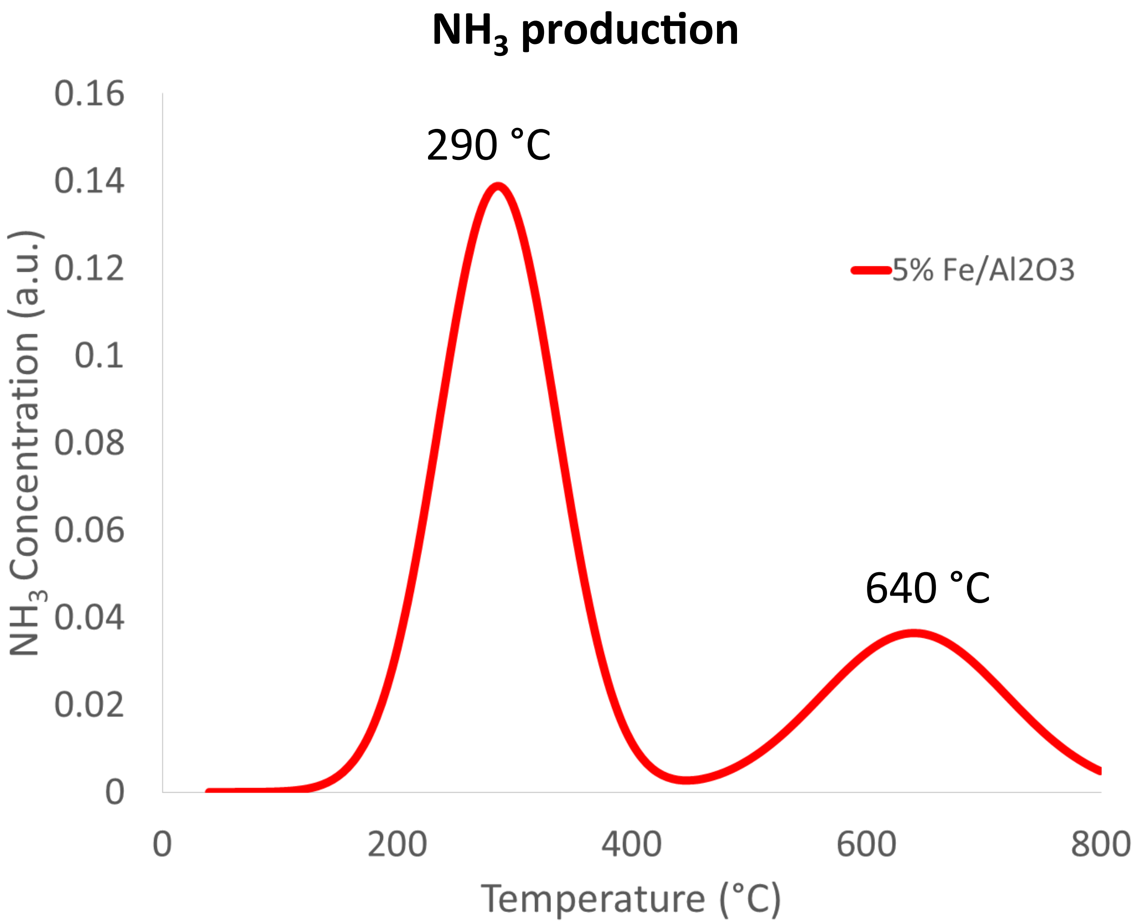
BET Surface Area Measurements

Catalyst	Surface Area ($m^2\ g^{-1}$)
Mo_2C	91
Fe/Mo_2C	65
Ru/Mo_2C	65
Co/Mo_2C	85
Mo_2N	159
Fe/Mo_2N	117
Ru/Mo_2N	126
Co/Mo_2N	132

- Nitrides tend to have higher surface area than carbides
- Depositing metal on the carbide and nitride retains the high surface area of the catalyst

Wyvratt, B. M.; Gaudet, J. R.; Thompson, L. T. *J. Catal.* **2015**, *330*, 280–287.

Comparing Nitrides to Carbides

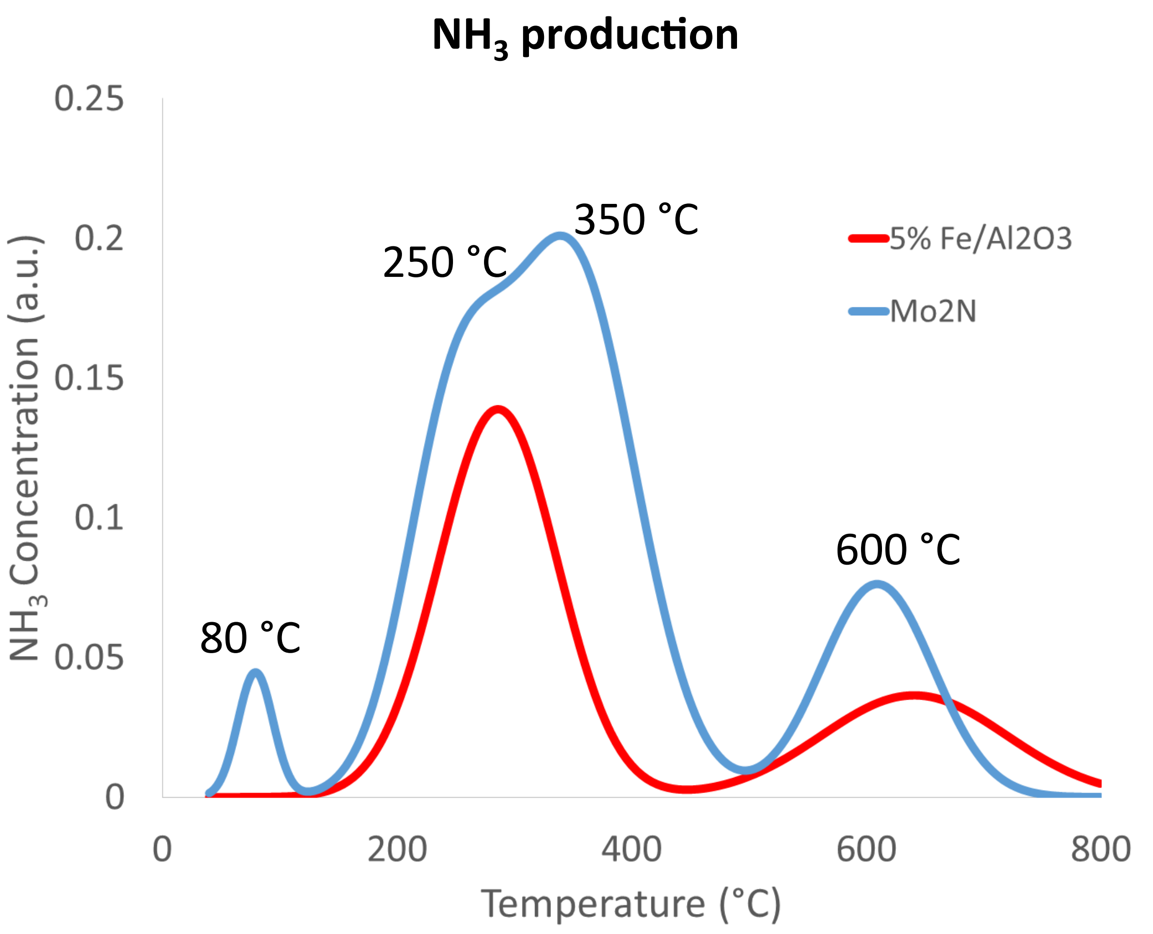


- Baseline was ran with N_2 and resulted in a flat line

Conditions:

- Mass of catalyst: ~100 mg
- Benchmark pretreatment: 3 hours, H2, 400 °C
- Nitride pretreatment: 1 hours, 25% N_2/H_2, 600 °C
- Carbide pretreatment: 4 hours, 15% CH_4/H_2, 590 °C
- Flow rate of reactants: 60 mL/min
- Temperature Ramp: 40 - 800 °C, 1 atm

Comparing Nitrides to Carbides



- Baseline was ran with N_2 and resulted in a flat line
- Mo_2N has an ammonia production site at 80 °C and higher production levels than the 5% Fe/Al_2O_3
- Four major sites for ammonia synthesis on bare Mo_2N

Conditions:
- Mass of catalyst: ~100 mg
- Benchmark pretreatment: 3 hours, H2, 400 °C
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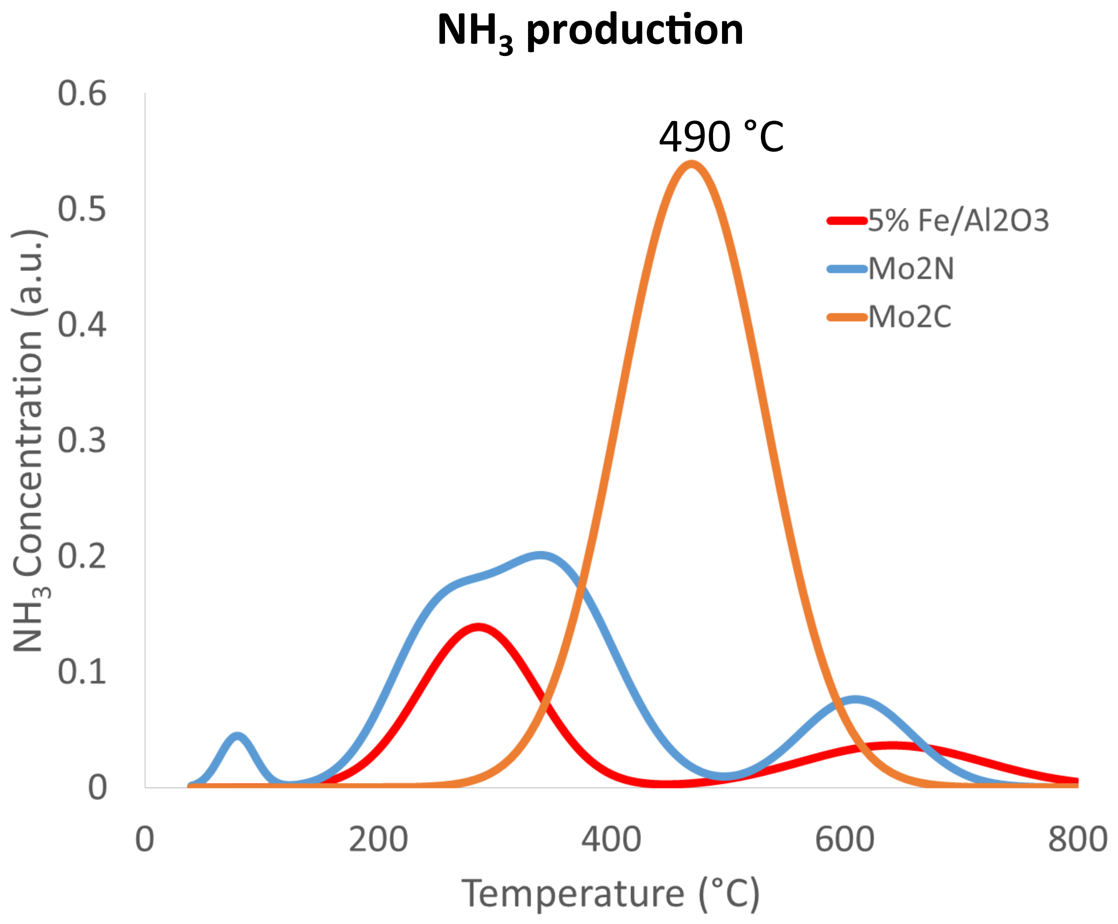

- Baseline was ran with N_2 and resulted in a flat line
- Mo_2N has an ammonia production site at 80 °C and higher production levels than the 5% Fe/$A_{l2}O_3$
- Four major sites for ammonia synthesis on bare Mo_2N
- High levels of ammonia production for bare Mo_2C at high temperatures

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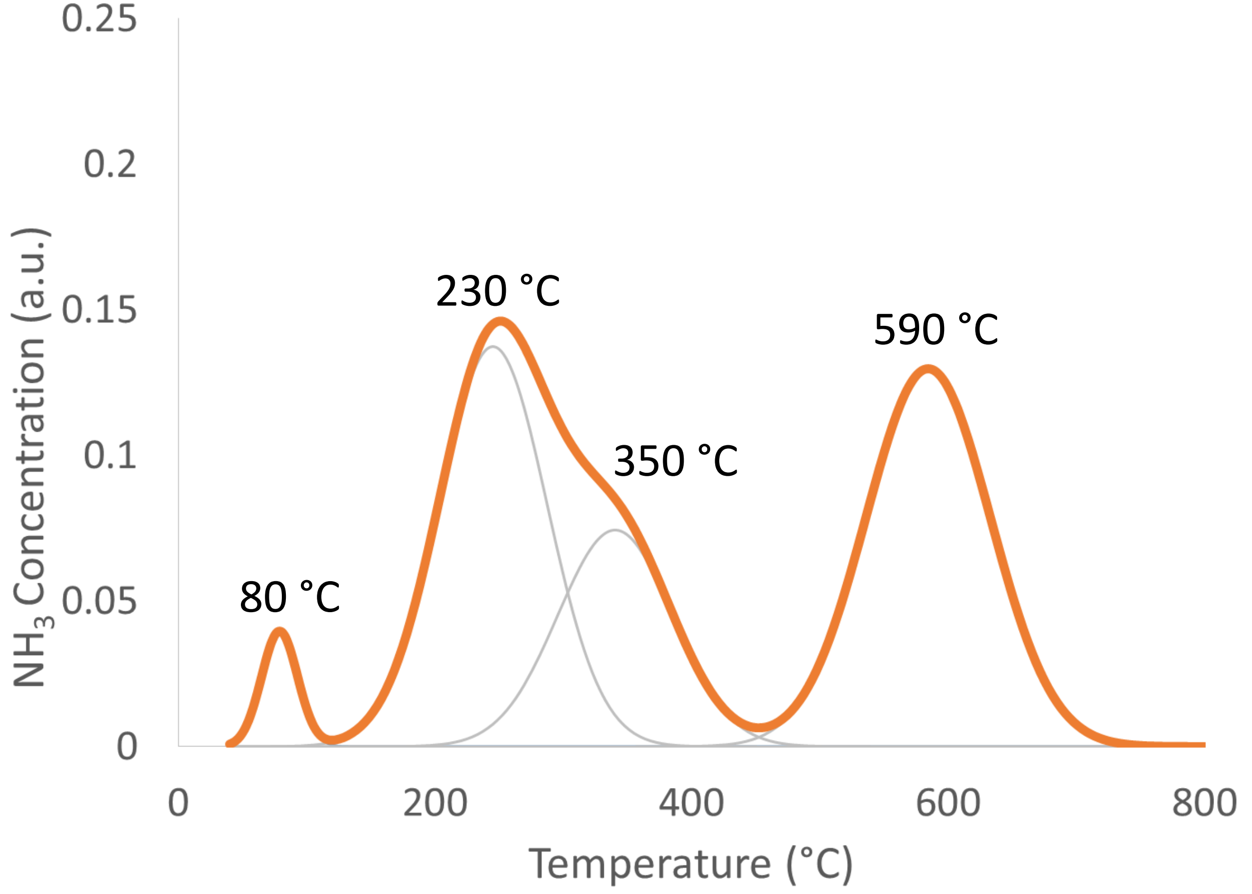
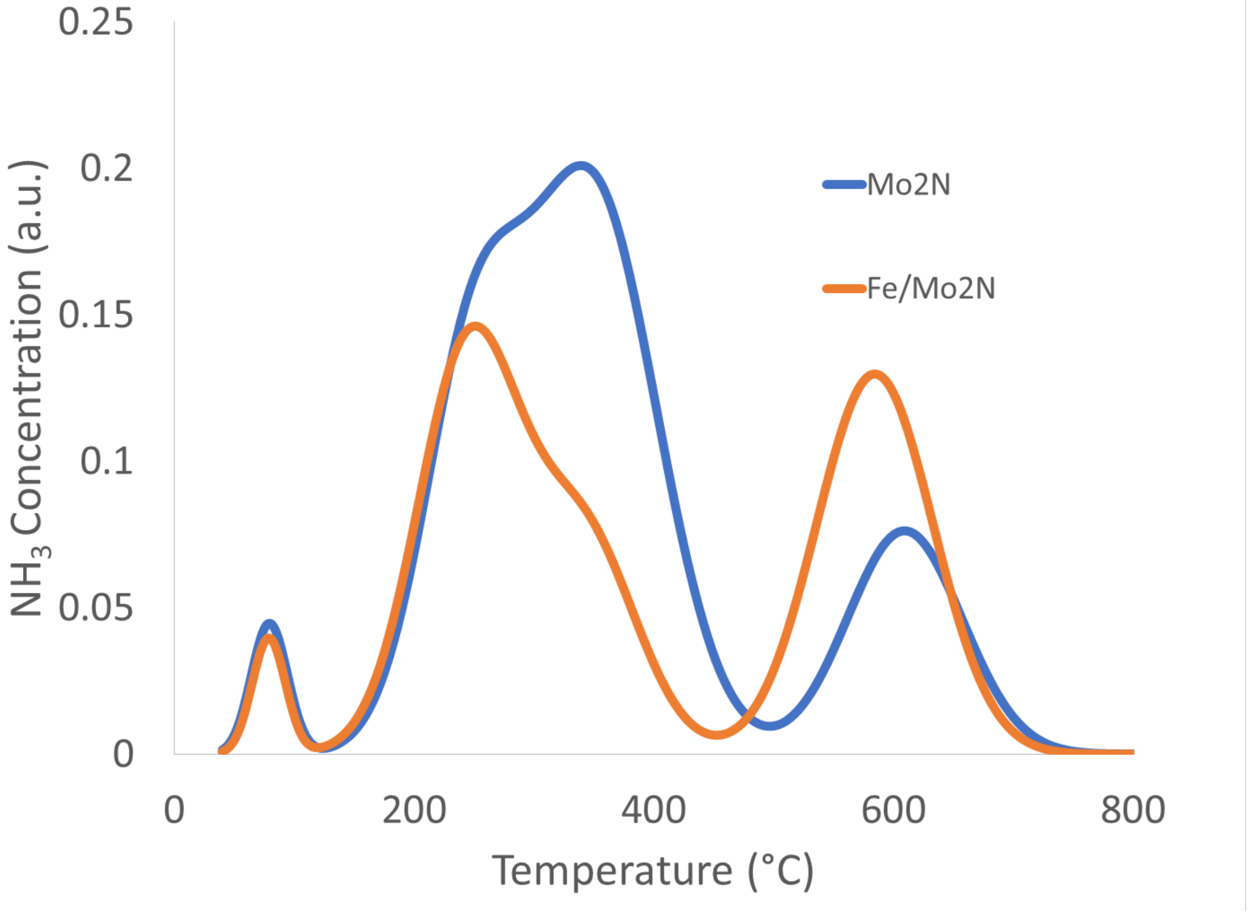
Catalyst Performance – M/Mo_2N

Fe/Mo_2N



Comparison M/Mo_2N



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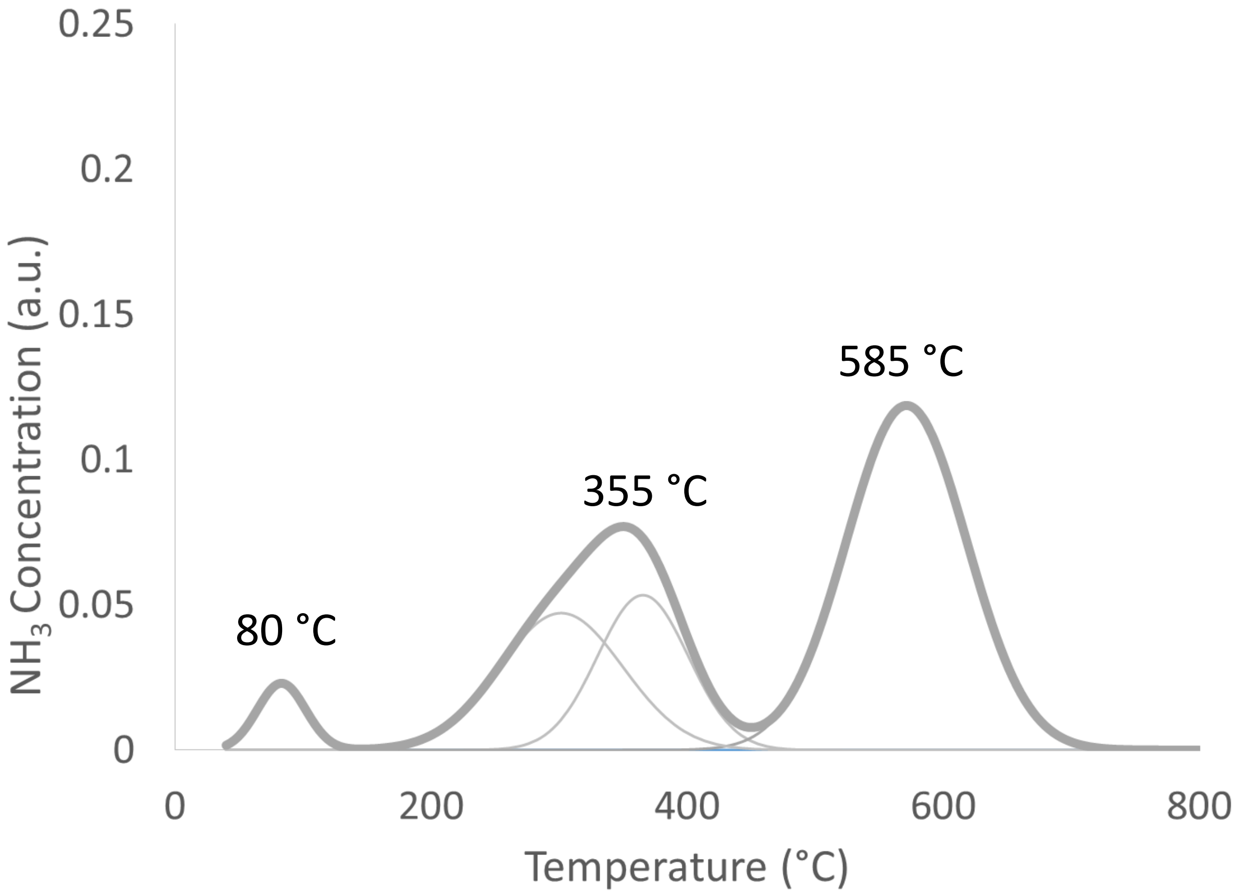
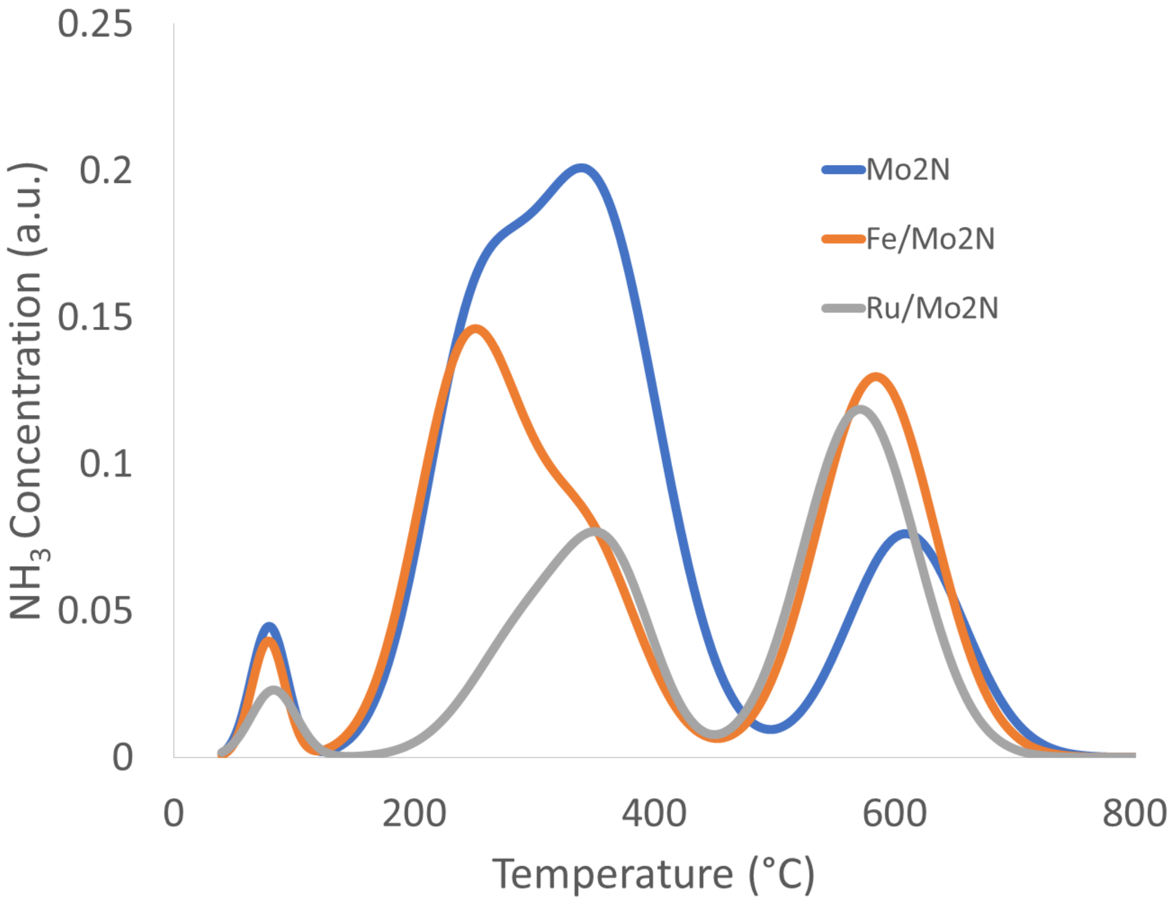
Catalyst Performance – M/Mo_2N

Ru/Mo_2N



Comparison M/Mo_2N



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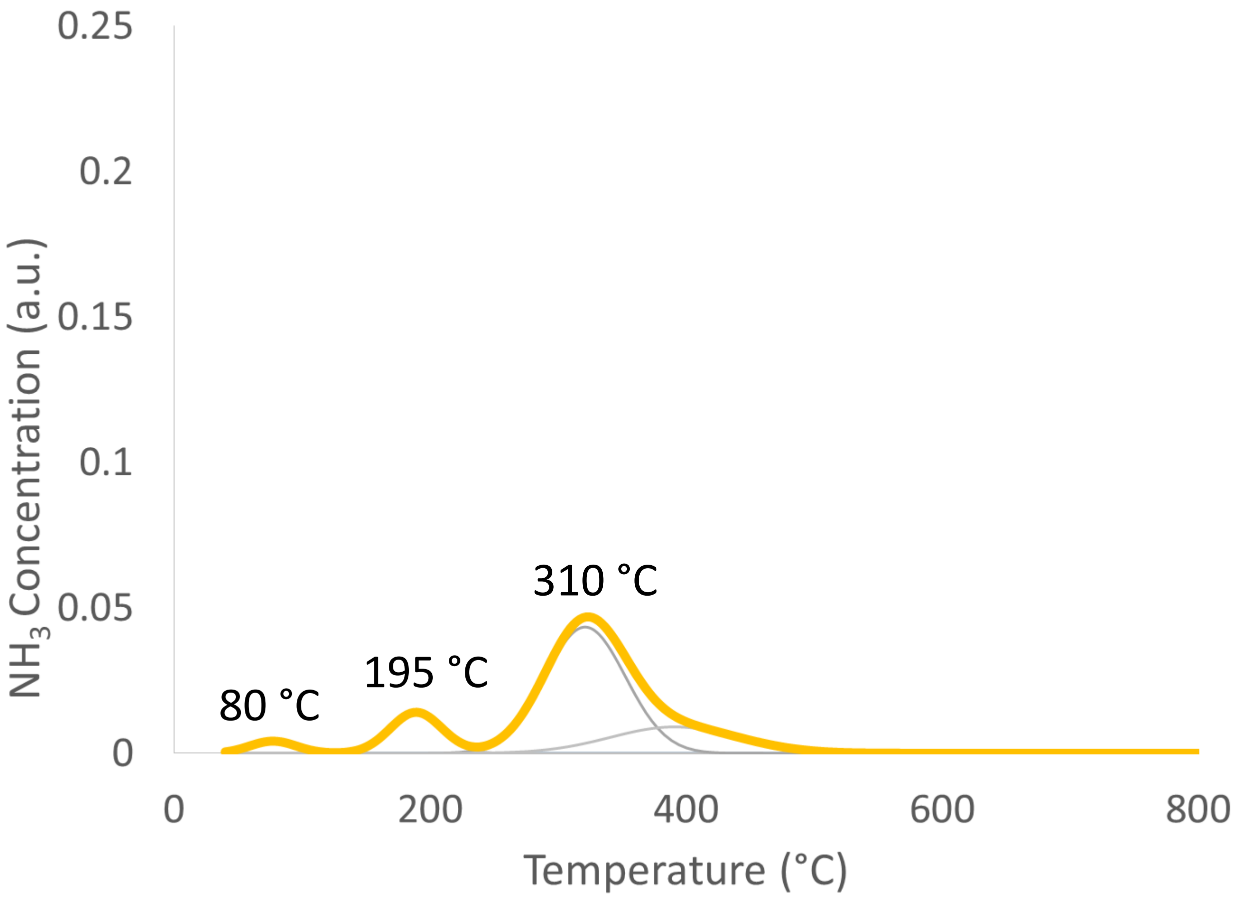
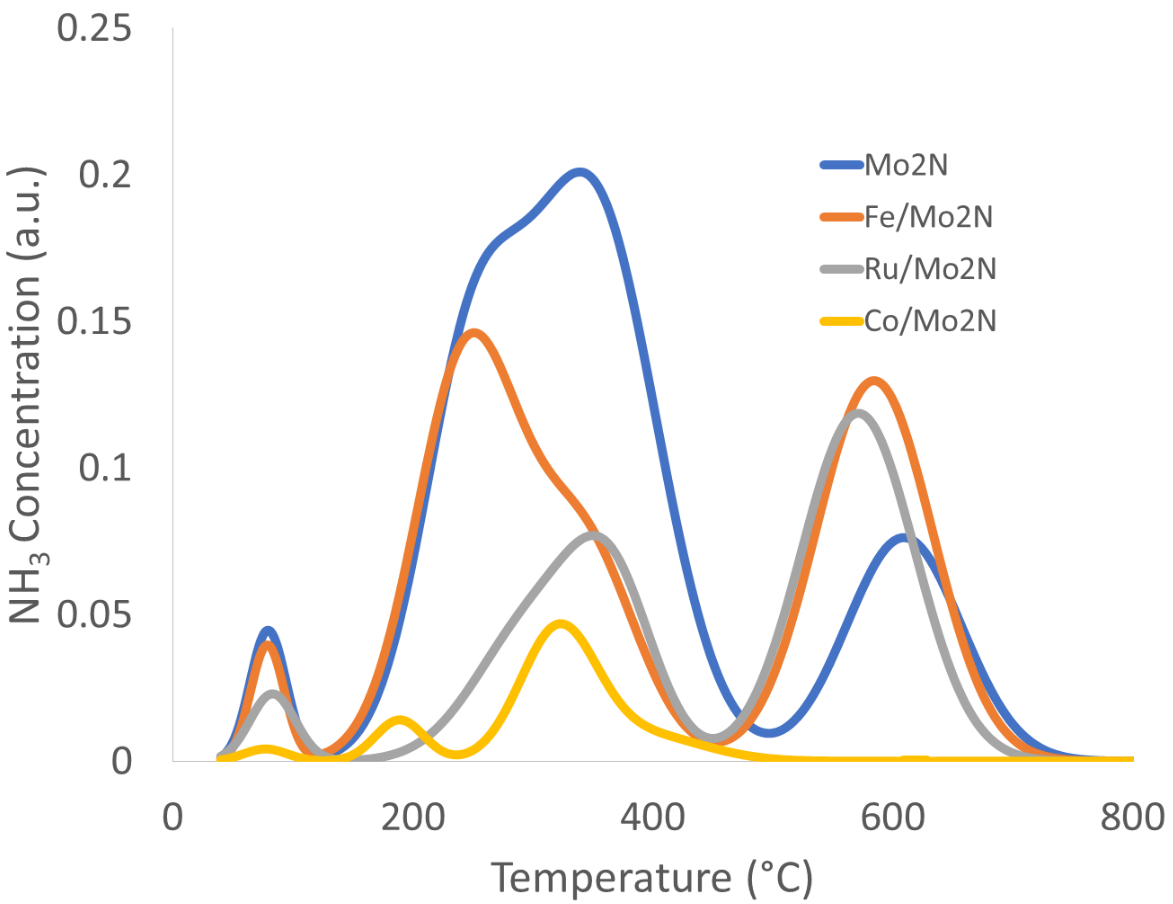
Catalyst Performance – M/Mo_2N

Co/Mo_2N



Comparison M/Mo_2N



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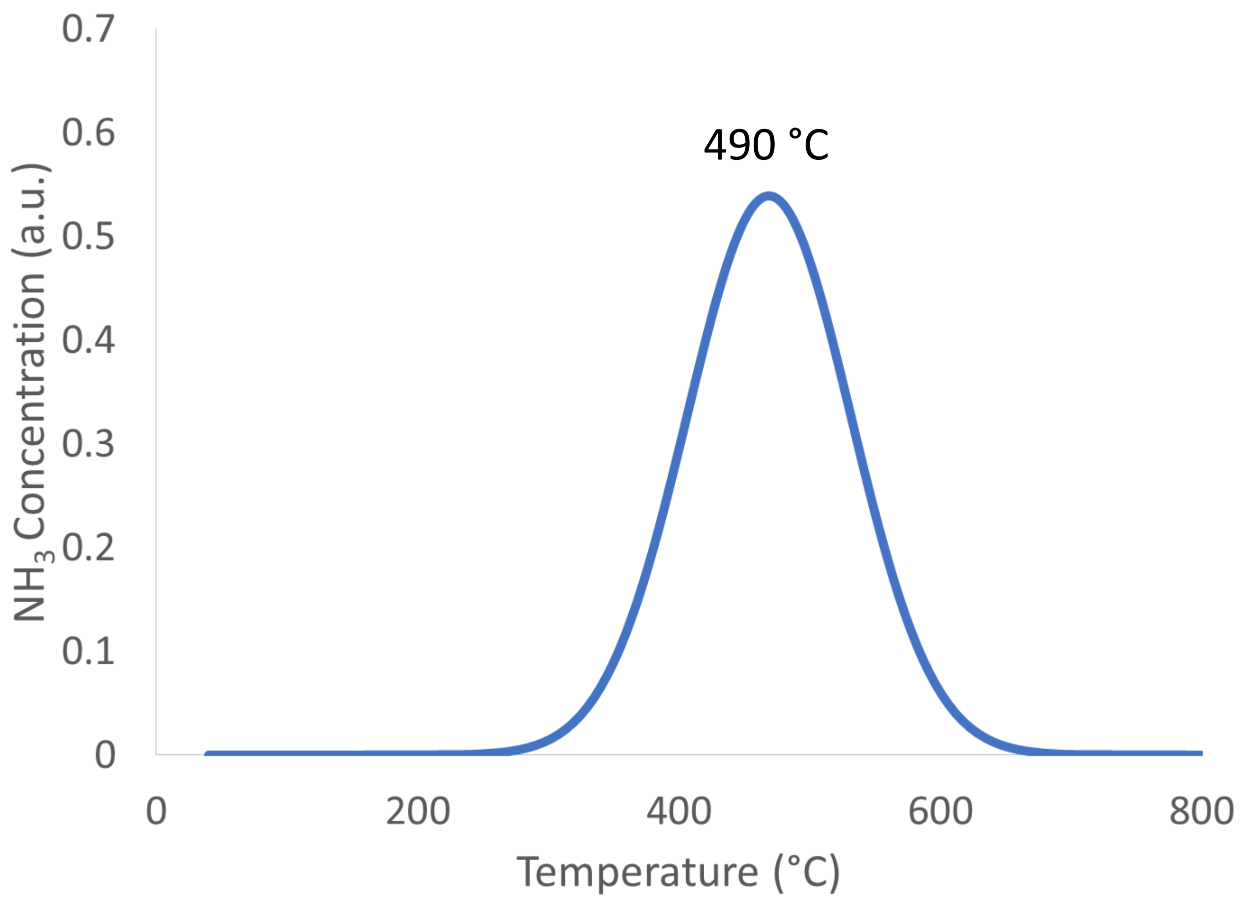
Catalyst Performance – M/Mo_2C

Mo_2C



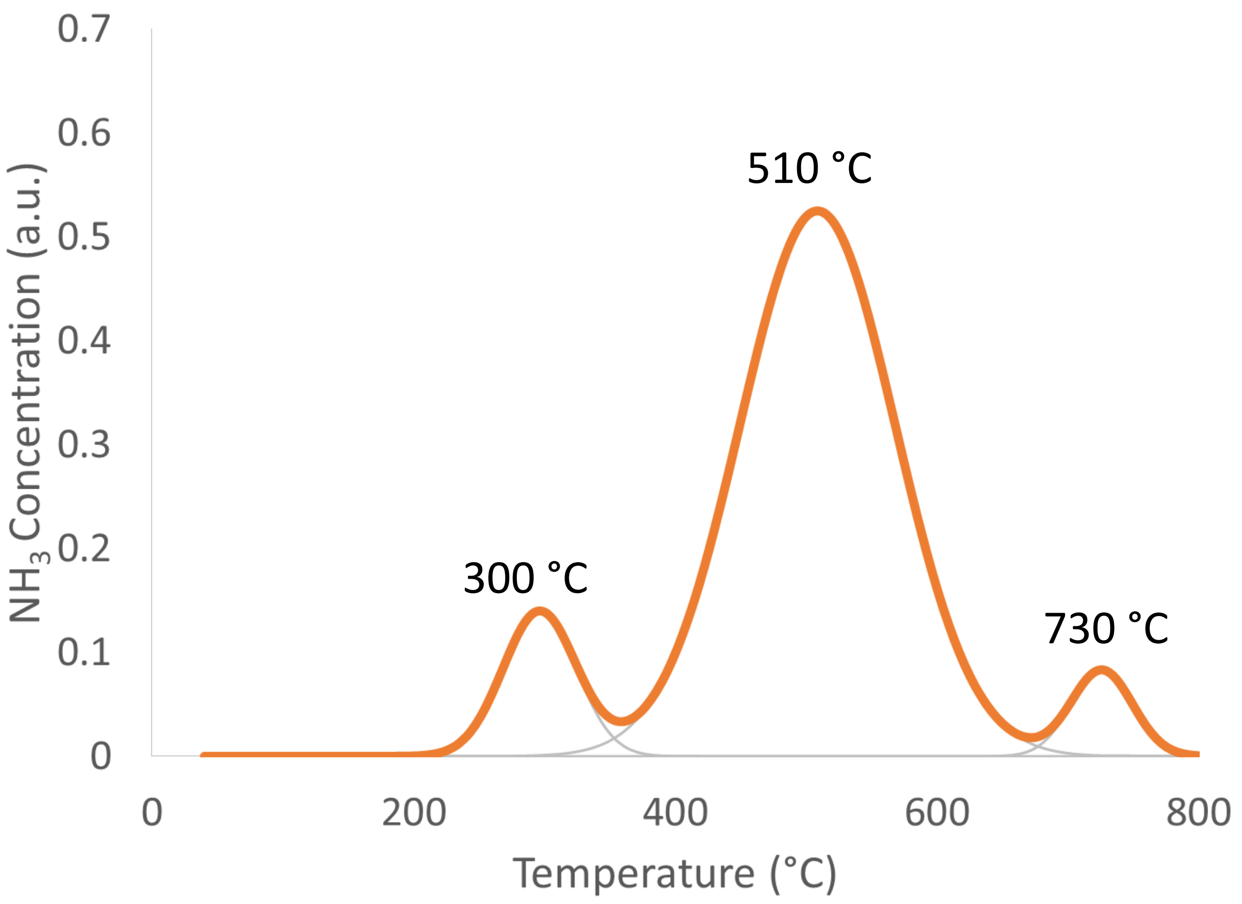
- Mo_2C does not display ammonia production at lower temperatures but it shows higher rates at typical reaction temperatures

Conditions:

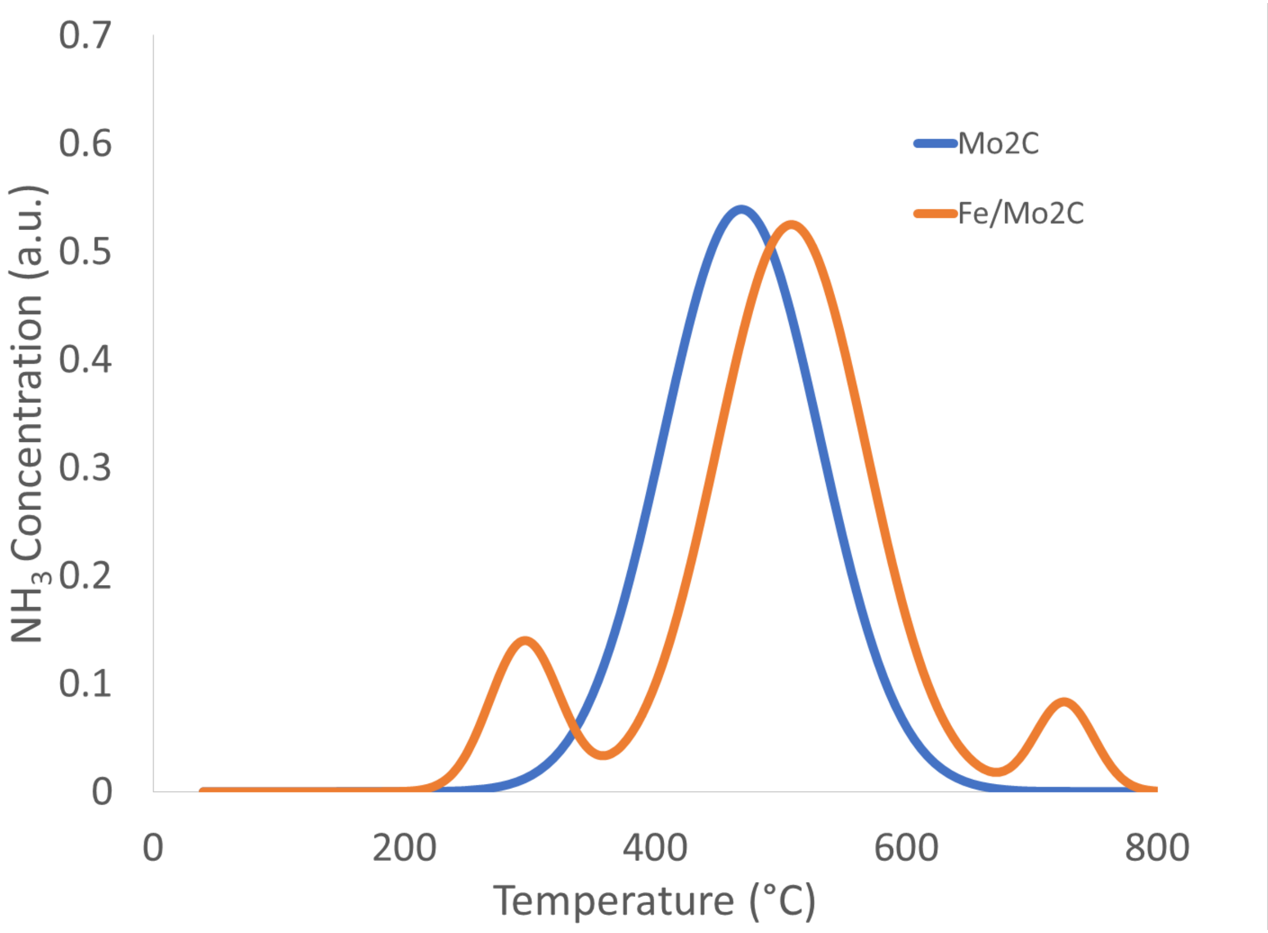
- Mass of catalyst: ~100 mg
- Carbide pretreatment: 4 hours, 15% CH_4/H_2, 590 °C
- Flow rate of reactants: 60 mL/min
- Temperature Ramp: 40 - 800 °C, 1 atm

Catalyst Performance – M/Mo_2C

Fe/Mo_2C



Comparison M/Mo_2C



Conditions:

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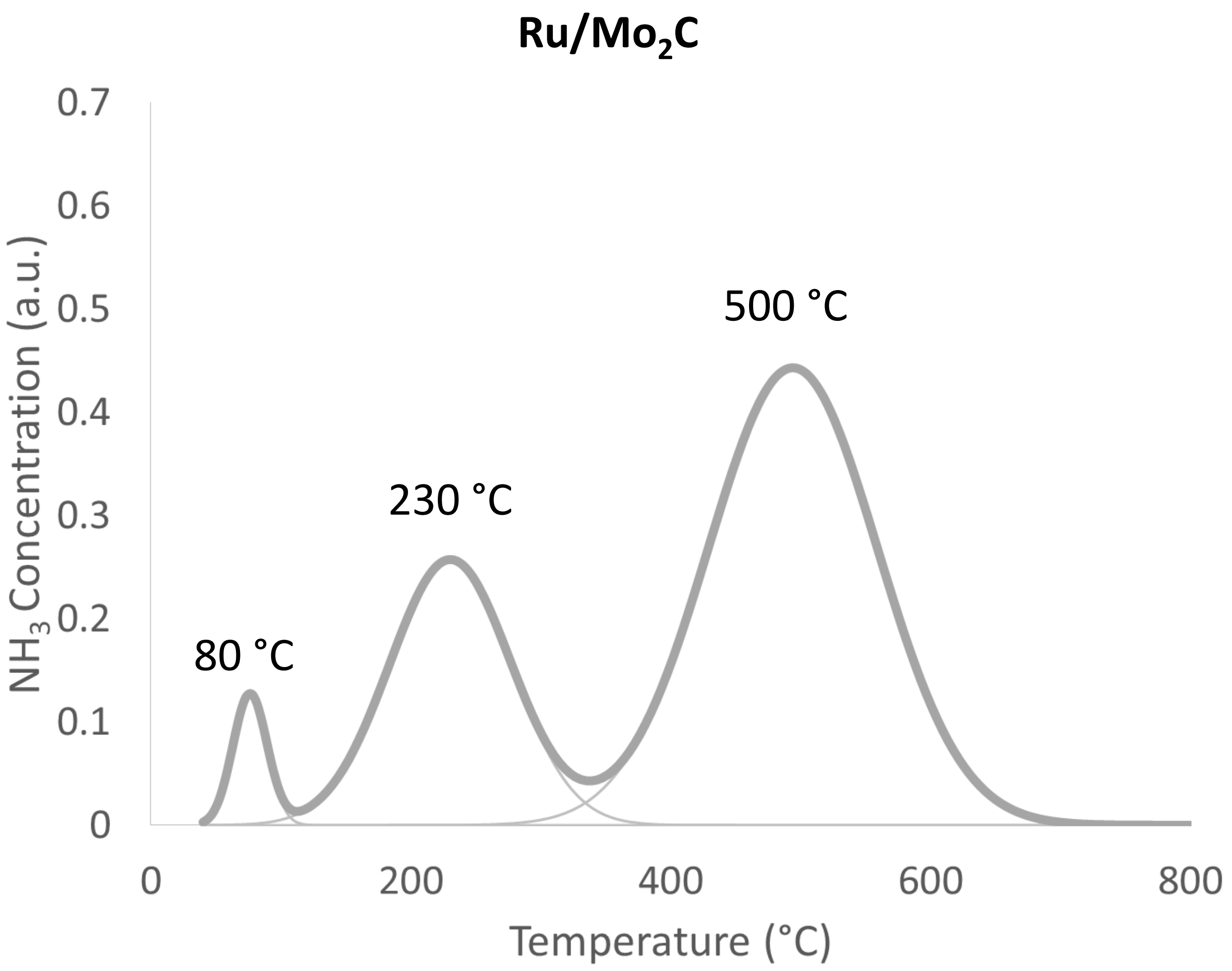
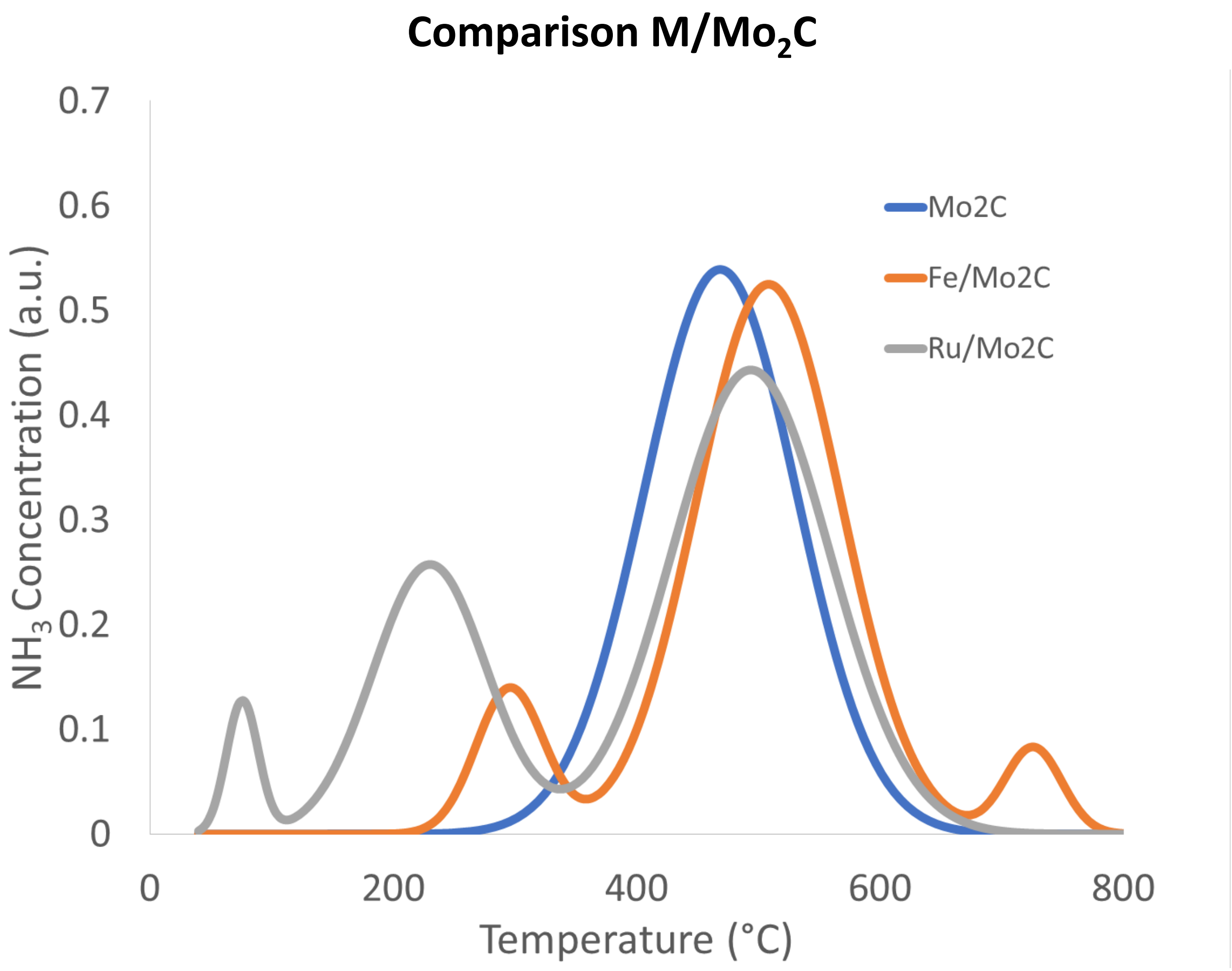
Catalyst Performance – M/Mo_2C





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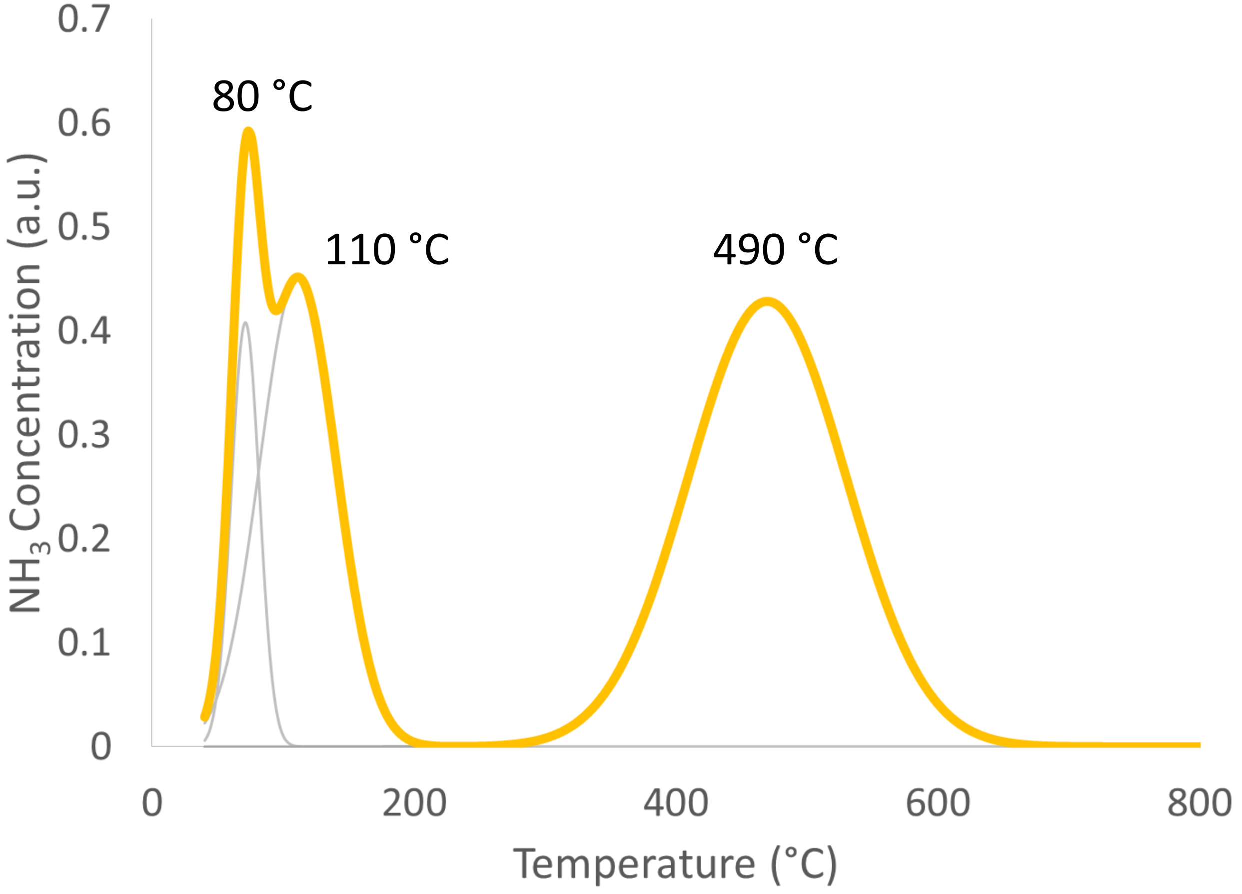
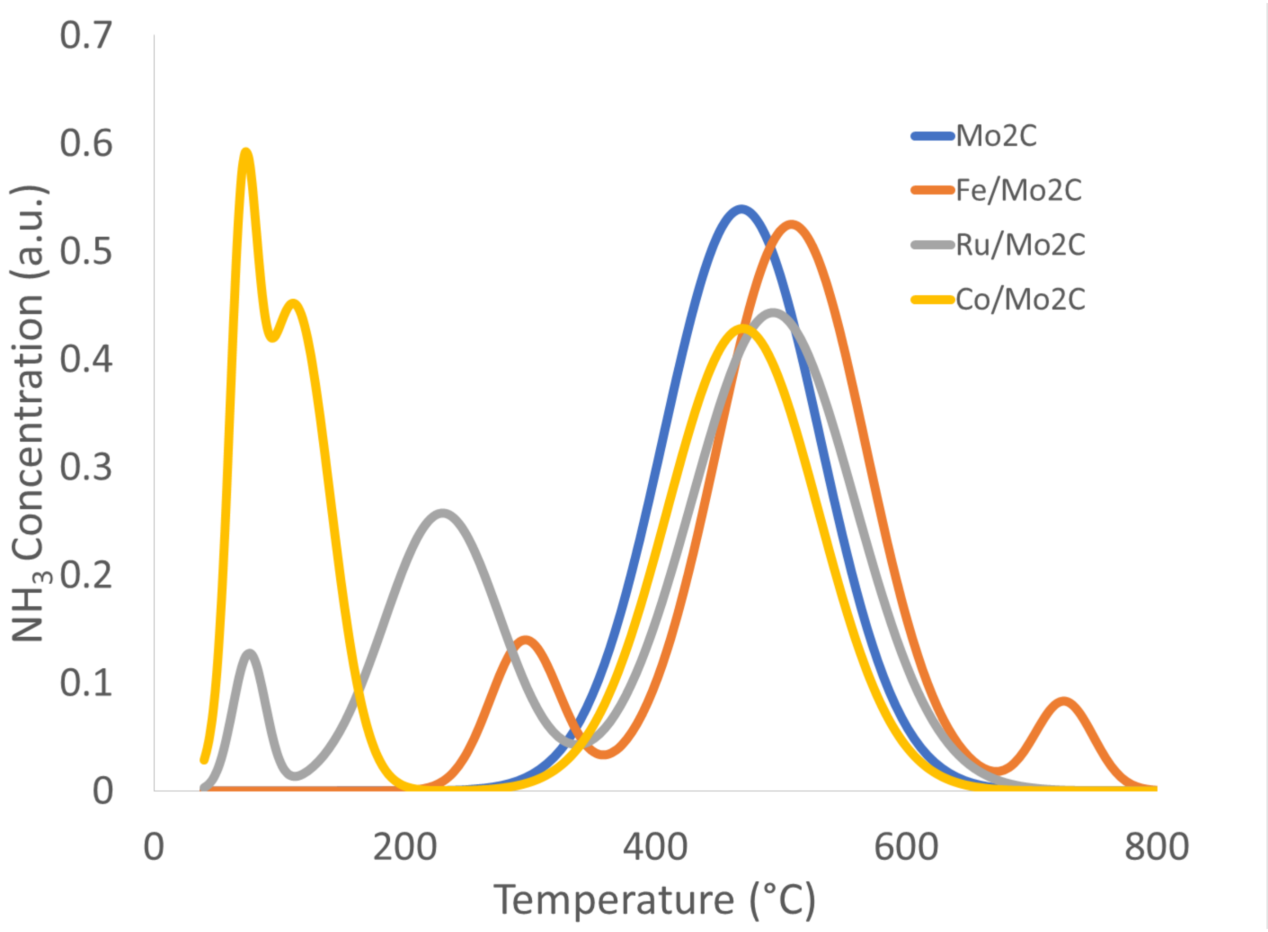
Catalyst Results – M/Mo_2C

Co/Mo_2C



Comparison M/Mo_2C



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- Flow rate of reactants: 60 mL/min
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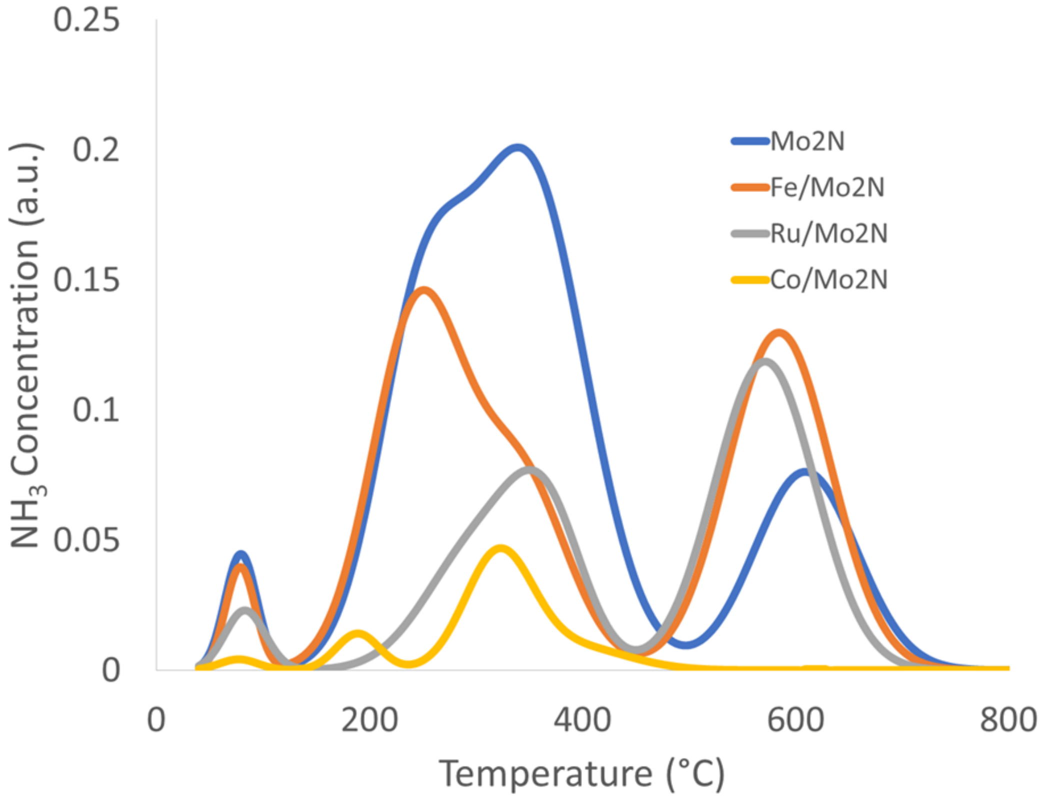
Conclusion

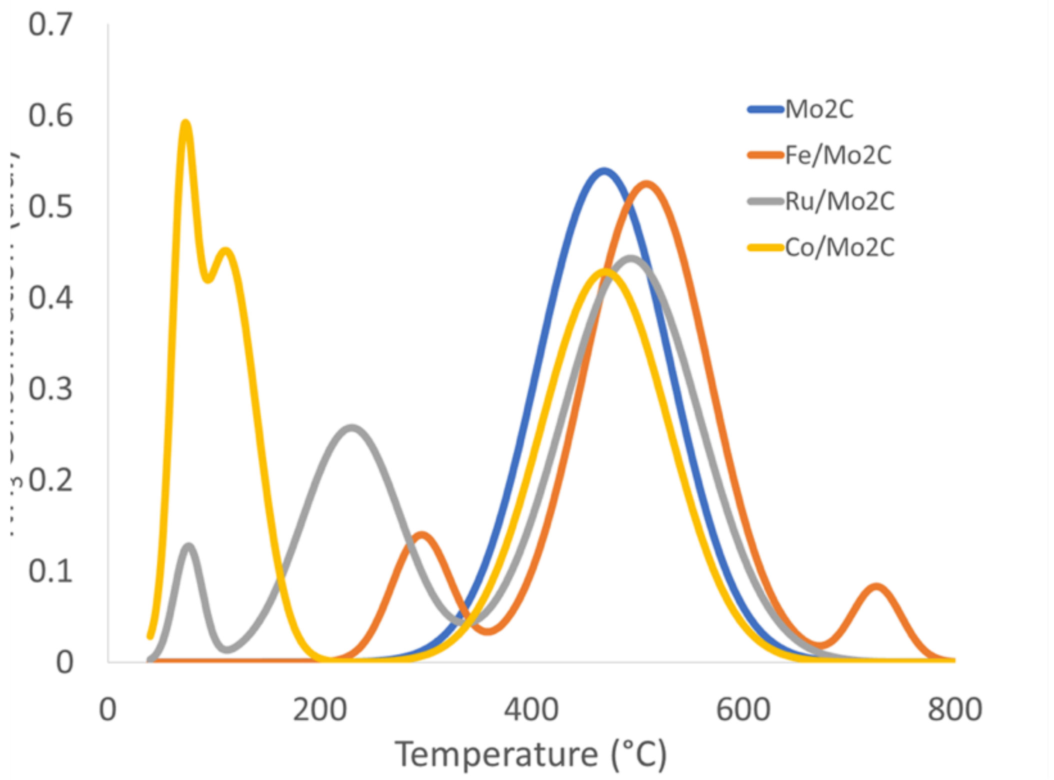
Confirm hypothesis:

- Bare Mo_2N are better than bare Mo_2C at temperatures as low as 80 °C
- Metals deposited on Mo_2N affected different types of sites
- Deposition of the metal on Mo_2C produced two new active sites for ammonia synthesis
- Co/Mo_2C is the most promising catalyst for low temperature ammonia production

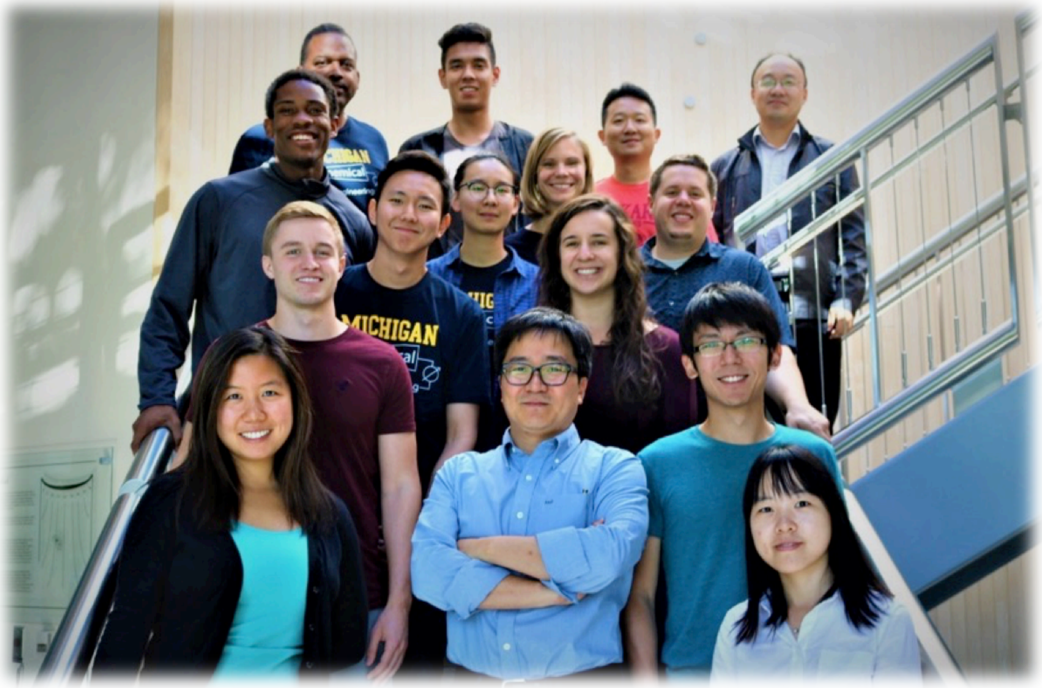
Future works:

- Kinetic studies of promising catalysts in flow reactor





Acknowledgements



NDSEG

Wei-Chung Wen
Sarah Paleg

Thompson Group

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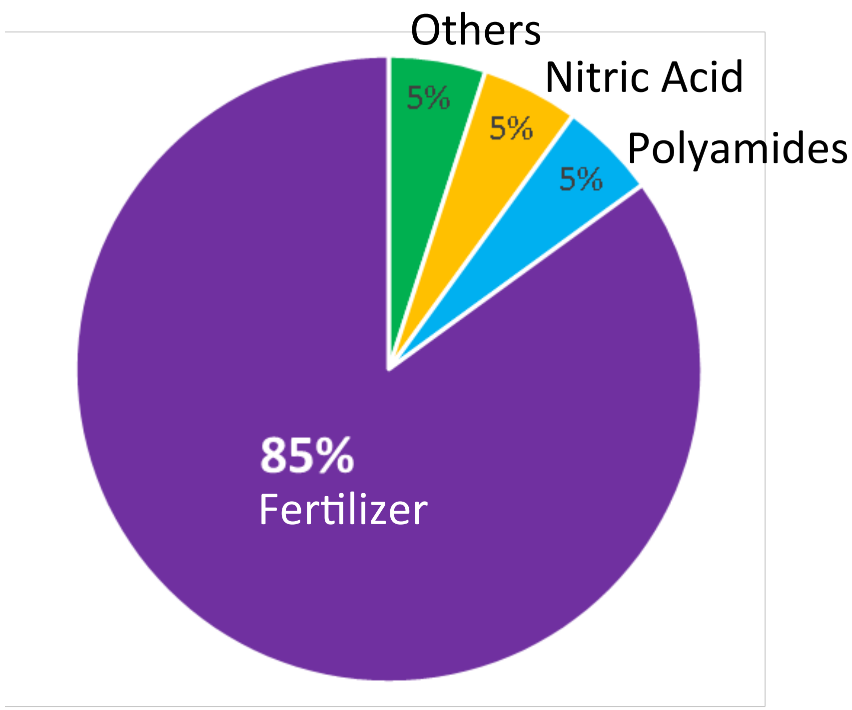
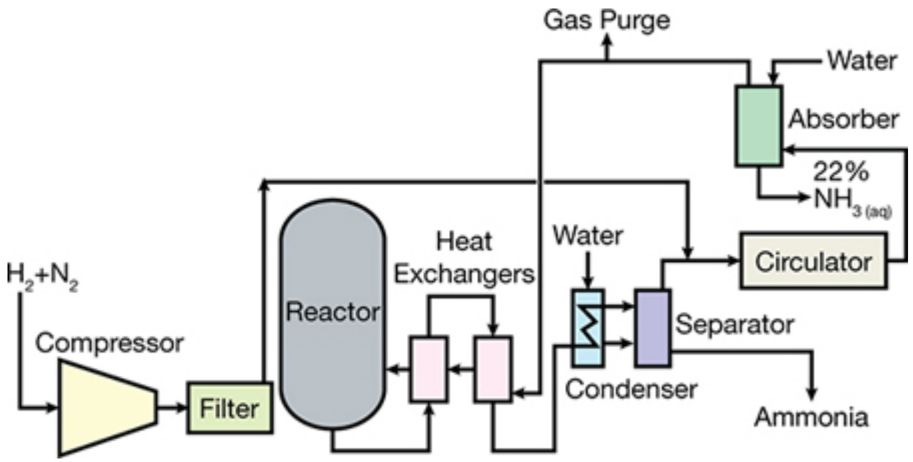
Questions?

Ammonia Synthesis

$$N_2 + 3H_2 \rightarrow 2NH_3$$





- Temperature: 400 – 500 °C
- Pressure: 150 – 300 bars
- Catalyst: Fe-based Al_2O_3

- In spite of developing insight in the field, industrial standards are still the same as those discovered at the beginning of the 20th century [1]

[1] Nørskov, J.; Contacts, B.; Miranda, R.; Fitzsimmons, T.; Stack, R.; Singh, A.; Rohr, B.; University, S.; Goldstein, J. **2016**.
[2] Uses for Ammonia, CIEC Promoting Science at the University of York, York, UK **2014**.
[3] Pattabathula, V, Richardson, J. *CEP* **2016**.

Catalyst Designs

Ternary Nitride Synthesis [1]

Molybdenum Precursor

Metal Impregnation

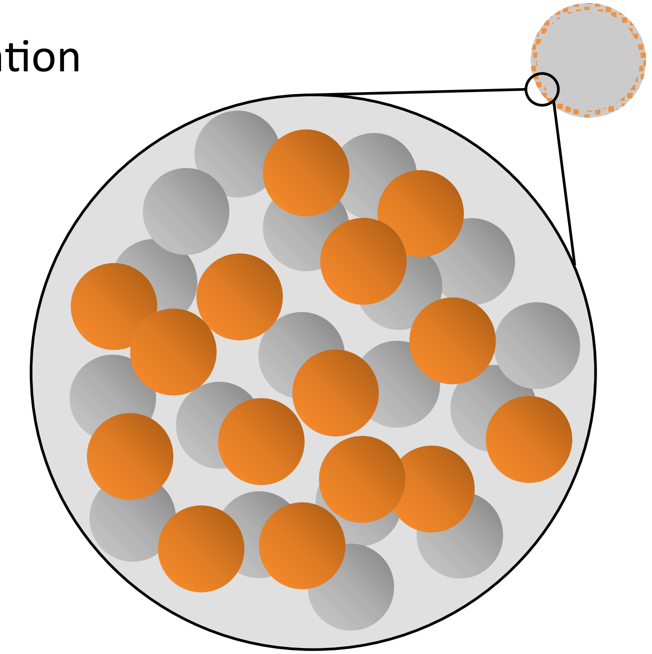
Nitridization

Metal-Loading Synthesis [2]

Molybdenum Precursor

Nitridization

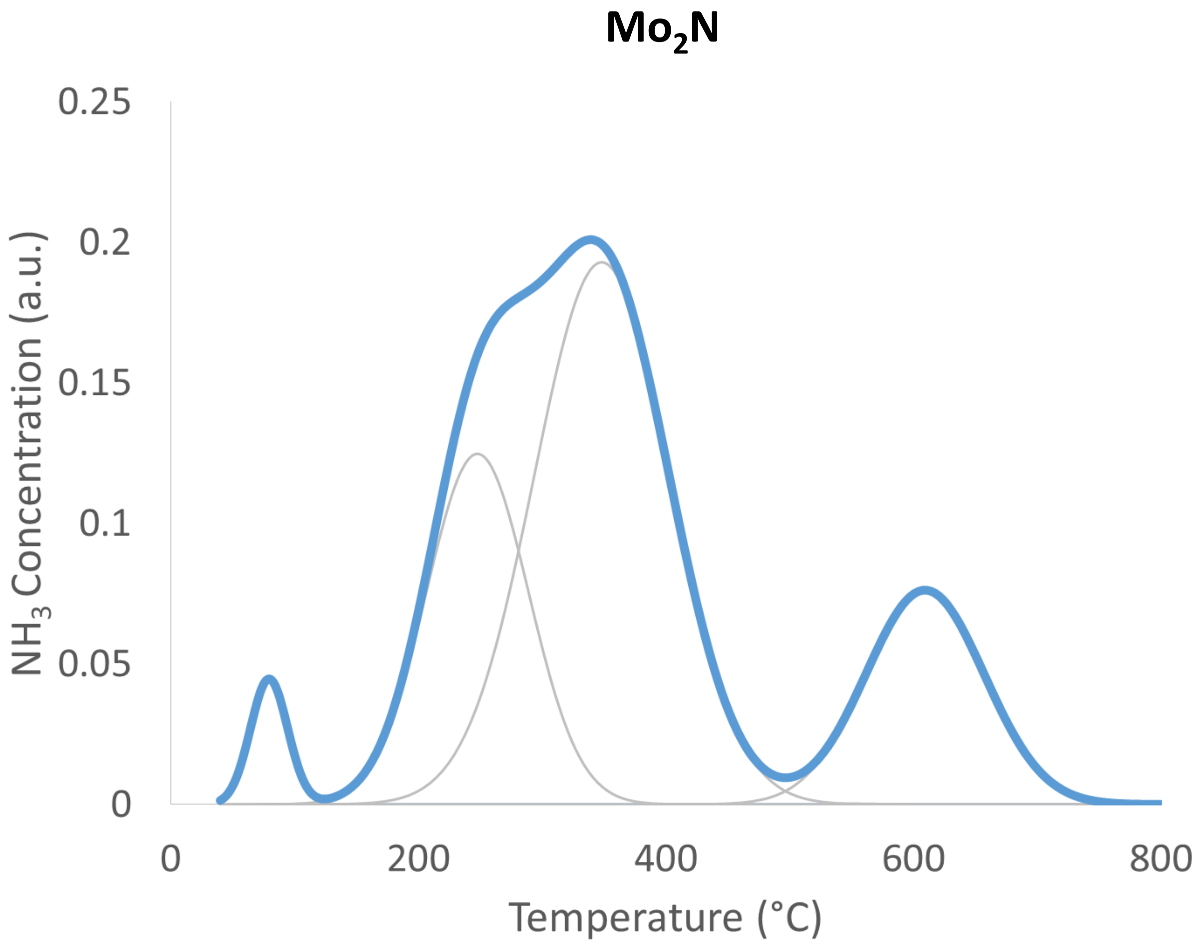
Metal Impregnation



Bifunctional active sites
on the surface

[1] Mckay, D. et al, *J. Solid State Chem.* **2008**, *181* (2), 325–333.
[2] Schweitzer, N. M.; Schaidle, J. A.; Ezekoye, O. K.; Pan, X.; Linic, S.; Thompson, L. T. *J. Am. Chem. Soc* **2011**, *133*, 2378–2381.
[3] Jacobsen et al, *J. Am. Chem. Soc.* **2001**, *123* (34), 8404–8405.

Catalyst Performance – M/Mo_2N



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- Flow rate of reactants: 60 mL/min
- Temperature Ramp: 40 - 800 °C, 1 atm

- Mo_2N displays ammonia production at temperatures as low as 80 °C
- Optimal production levels between 200 – 400 °C → many of the experimental conditions might not be appropriate for this material