2018 DOE Vehicle Technologies Office

Next Generation SCR-Dosing System Investigation

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Project ID # ACS027

Project Overview

Vehicle Technologies Office

Timeline

- Start – Oct 2014
- End – Sept 18

Budget

- Matched 80/20 by USCAR as per CRADA agreement
- DOE funding for FY18: $100K;

Barriers

Addressed in next slide

Partners

- Pacific Northwest National Laboratory
- USCAR

Barriers - Relevance

- Selective Catalytic Removal of NO_x:

  $4\ NO + \mathbf{4\ NH_3} + O_2 \rightarrow 6\ N_2 + 6H_2O$

- SCR makes engines more efficient
- NOx reduction systems (SCR) will require **improved ammonia storage and low temperature delivery**.
- Needed for diesel and lean-burn engines
- Challenge: Safe and efficient ammonia storage and delivery

- Urea solution (DEFBlue or Adblue®) [Urea+ ~70% water] mitigates most issues

- New materials as needed to solve issues with aqueous urea
- Compact NH_3 storage coupled with long driving range will help minimize fuel consumption

NOx tail-pipe emission and USCAR FTP cycle

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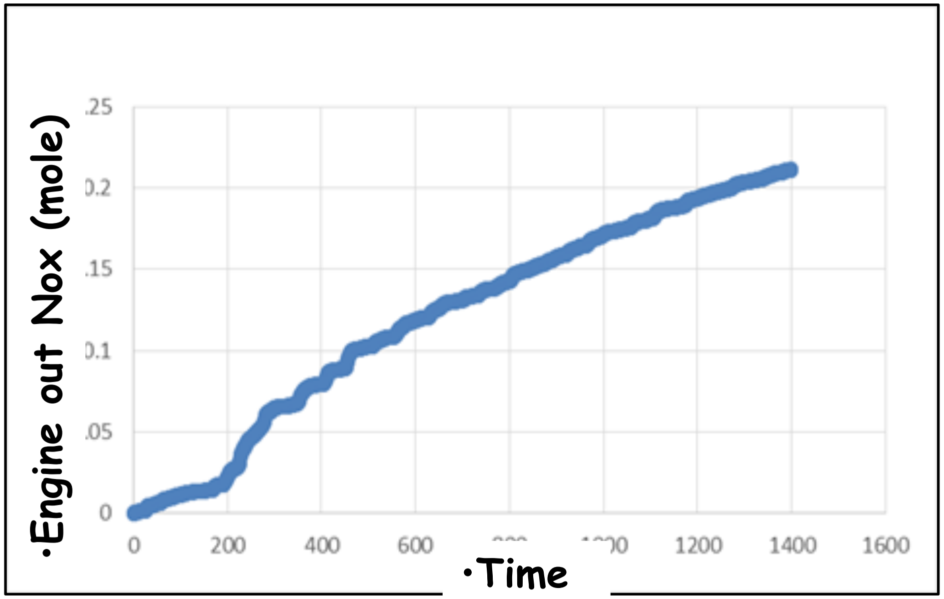


	USCAR FTP cycle
Total NH3	4.8 g
Avg. mass flow	3.1 mg/s
Peal flow	22.6 mg/s
Cycle length	1399 sec

Opportunity: Explore fuel economy improvement enabled by low-temperature dosing of ammonia gas.

Item	Unit	20 ºC	-7 ºC	-15 ºC
Start time	sec	<90	<123	<152
Total energy requirement	kJ	64	98	107
Peak power requirement	kW	0.2/0.3	0.2/0.3	0.2/0.3

Collaborations/Interactions

OEM

Development Teams and Suppliers

Project Management

PNNL

USCAR

•Provide results of current performance metrics of various NH_3 storage materials and feedback on material performance

PNNL

Carry out and disseminate results of synthesis, characterization, testing and provide recommendations to USCAR

- Monthly updates and teleconference with USCAR PI
- Quarterly teleconference with USCAR SCR team
- Bi-annual F2F meeting with USCAR SCR team

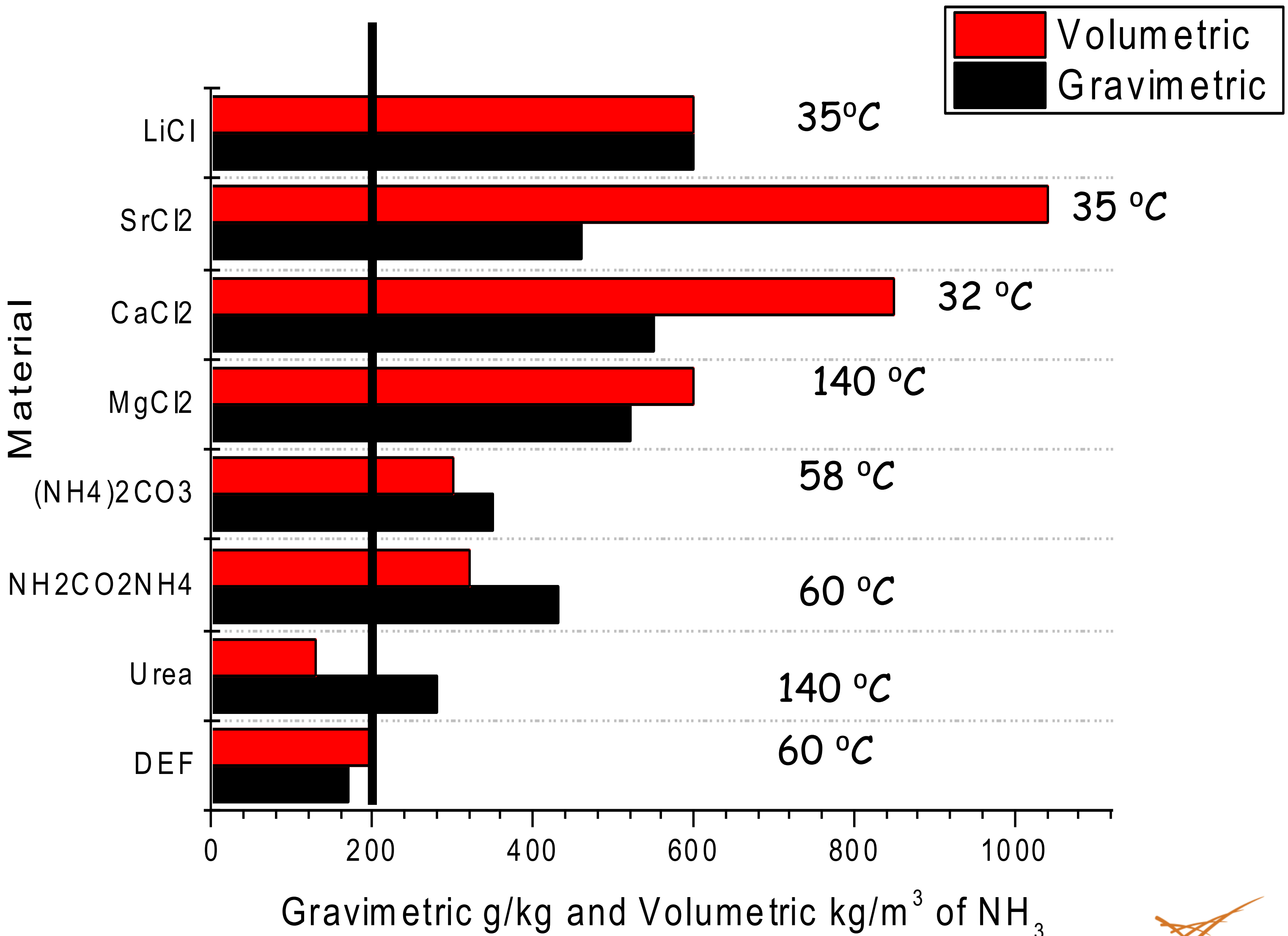
Goals and Objectives

- Develop alternative ammonia carrier materials for low temperature NH_3 dosing system
- 32.5 wt% aqueous Urea contains 17wt% NH_3 (gravimetric) and 200 kg/m^3 (volumetric): Any proposed materials should exceed these targets.
- Help develop the next generation SCR dosing system for improved low-temperature performance
- Convenient handling and distribution of ammonia carriers, and reduced overall system volume, weight, and cost

FEV solid SCR system: Ammonium carbamate

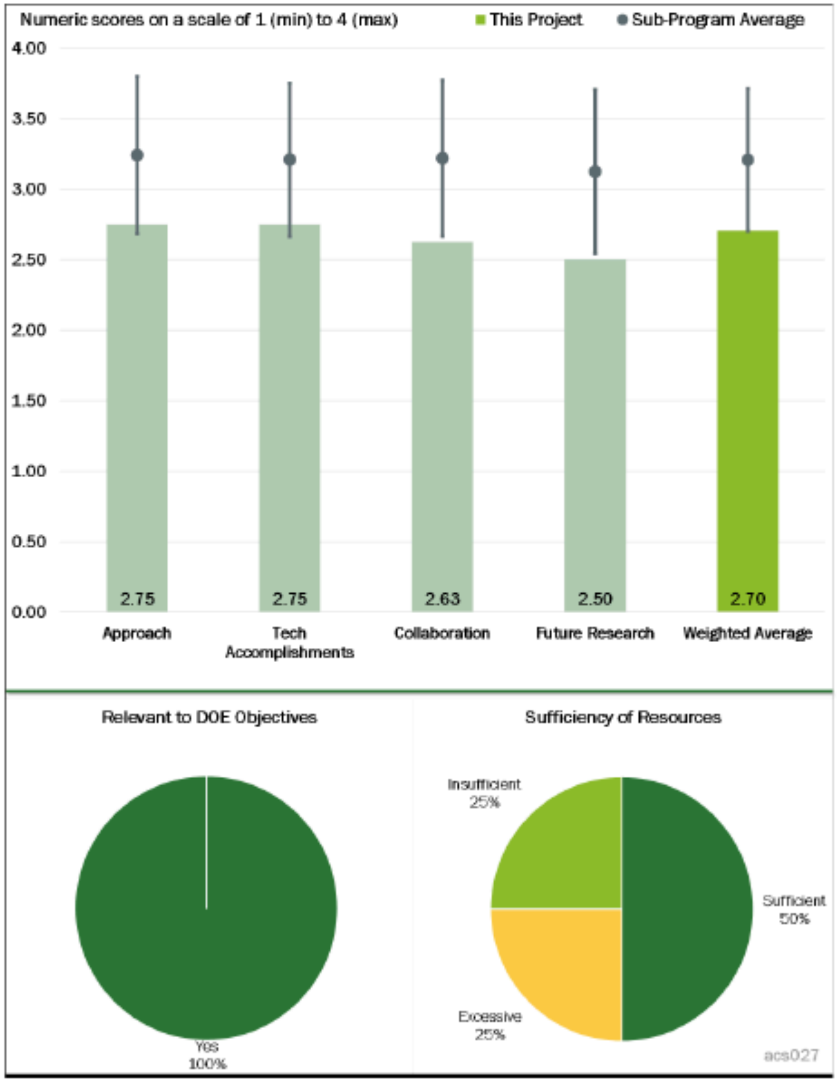
Liquid urea (DEF)

Summary of material properties



Reviewer Comments

- Project needs to consider non-chlorine materials that will not produce hydrogen chloride (HCl)
- The simplest thing would be to increase the exhaust temperature and continue to use the eutectic mixture of urea in H_2O
- The project as a solid accomplishment to downselect material that can perform properly without significant increase in volume.



Response to Reviewer Comments

- HCl: We focused on efforts to switch to light weight metal oxides
- We studied the potential of a novel concept developed to enhance ammonia sorption
- We will continue to evaluate other oxide based materials for the remainder of the year

Approach

- Evaluate existing materials based on USCAR recommendations
- Synthesize new materials and composites to improve on existing materials

Develop testing protocol to:

- Determine ammonia storage capacity: wt.%/vol.%
- Determine ammonia release: temp, rate, energy requirement
- Solid material volume change during charge/discharge
- Stability and Safety: volatility under storage & handling conditions extended temp.
- Utilize expertise and state-of-the-art characterization and testing facilities at PNNL to address structure/function and performance
    - XRD, NMR, NH_3 TPD, DSC-TGA with MS
    - Time resolved FTIR studies for kinetics
    - Calorimetric studies for thermodynamics
    - Volumetric gas analyzer for vapor pressure studies

Impurity Quantification and Mitigation: HCl Measurements

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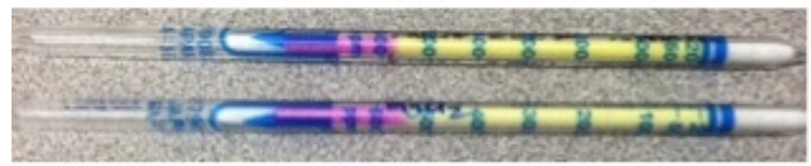
Material (Quantity, g)	Time (hr)	Temperature* (°C)	Amount of HCl (ppm)
$MgCl_2$	3	400	~550
$MgCl_2$	24	400	>600
$MgCl_2$	24	400	>600
$MgCl_2$	100	400	>600
$MgCl_2$	24	400	~580
$Mg(NH_3)_6Cl_2$	24	250	20
$MgCl_2$:AC (2:1)	24	600	>600
$Mg(NH_3)_6Cl_2$:AC (1:1)	24	400	No HCl
$Mg(NH_3)_6Cl_2$:AC (1:1)	24	400	No HCl
$Mg(NH_3)_6Cl_2$:AC (2:1)	24	250	No HCl
$Mg(NH_3)_6Cl_2$:KBB (3:1)	24	250	No HCl

KITAGAWA Gas Detection Tubes



Successful mitigation of HCl by development of composites

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DEFBlue™ Vs. $MgCl_2.6NH_3$

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DEFBlue™

- 30% Urea +70% Water
- 200 kg NH_3/m^3
- 17 wt% NH_3 (on composition basis)
- Convenient
- Freezing
- Solid deposits
- Lowering of exhaust temp due to water

$MgCl_2.6NH_3$

- ~ 600 kg NH_3/m^3
- 50 wt% NH_3 (on composition basis)
- Multi-step decomposition
- No complex chemistry
- Easily available $MgCl_2$ (10% of sea salt) and NH_3
- Freezing a non-issue

We will use DEF to benchmark our materials

Recent Accomplishments

- Characterize and Study the NH_3 uptake capacity of the Eutectic salts.
- In order to eliminate HCl we focused on developing oxide based materials
- Evaluated ammonia storage capacity of oxide based materials
- Synthesized and developed solid solution based materials for screening NH3 uptake and release

CO_2 absorption on MgO Eutectics

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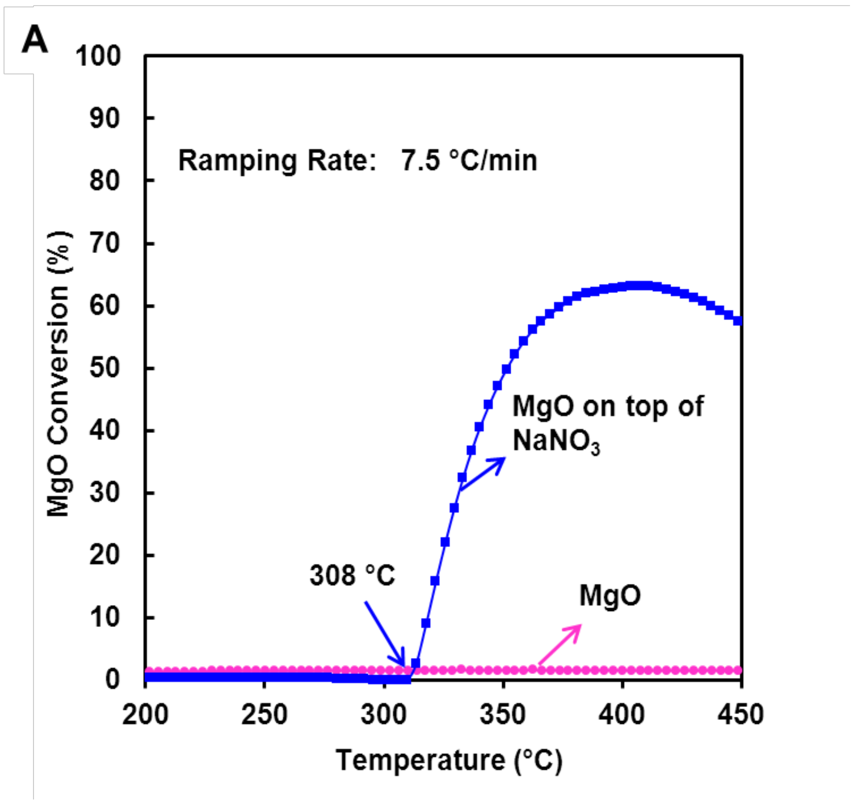

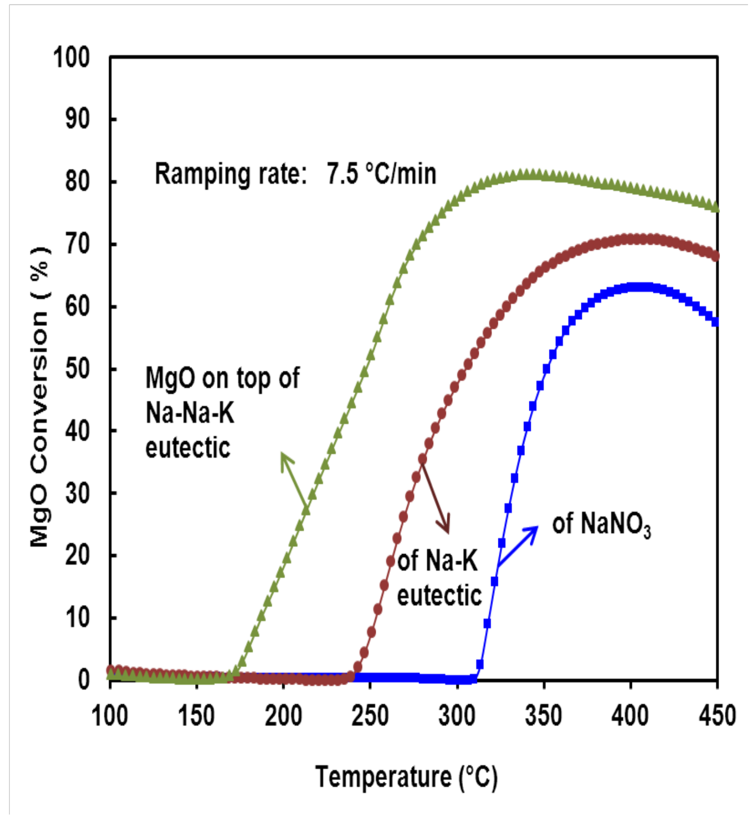

- CO_2 absorption on MgO with $NaNO_3$
- Decrease in temperature of CO_2 uptake

- CO_2 absorption on MgO with various salts
- Ability to tune temperature of CO_2 uptake

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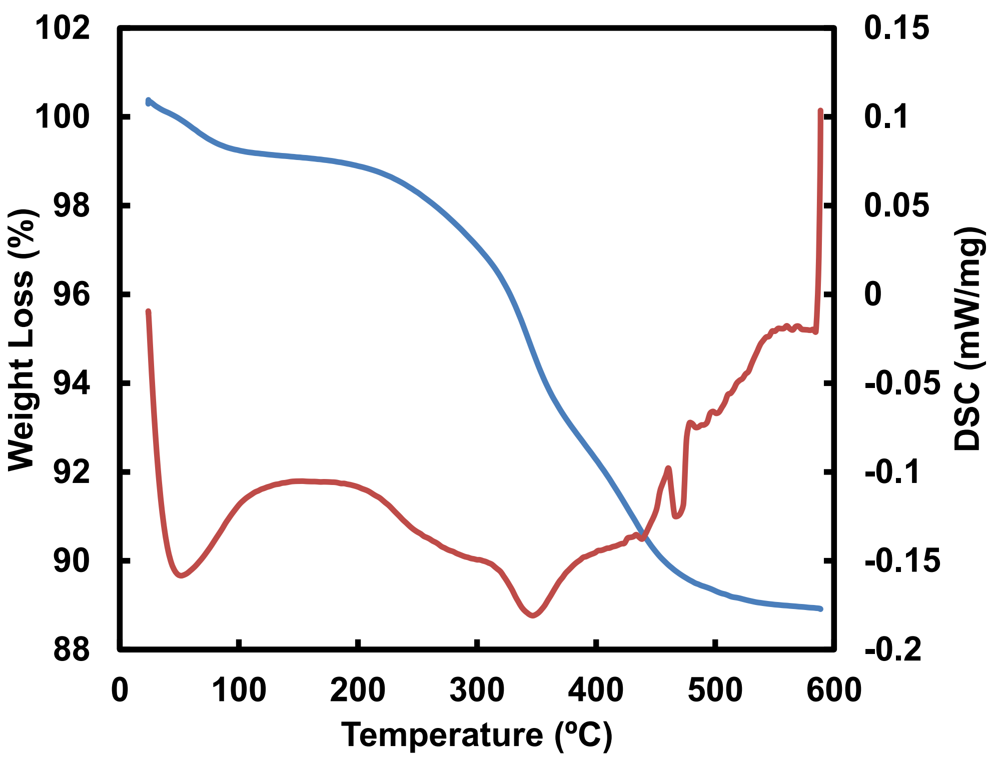
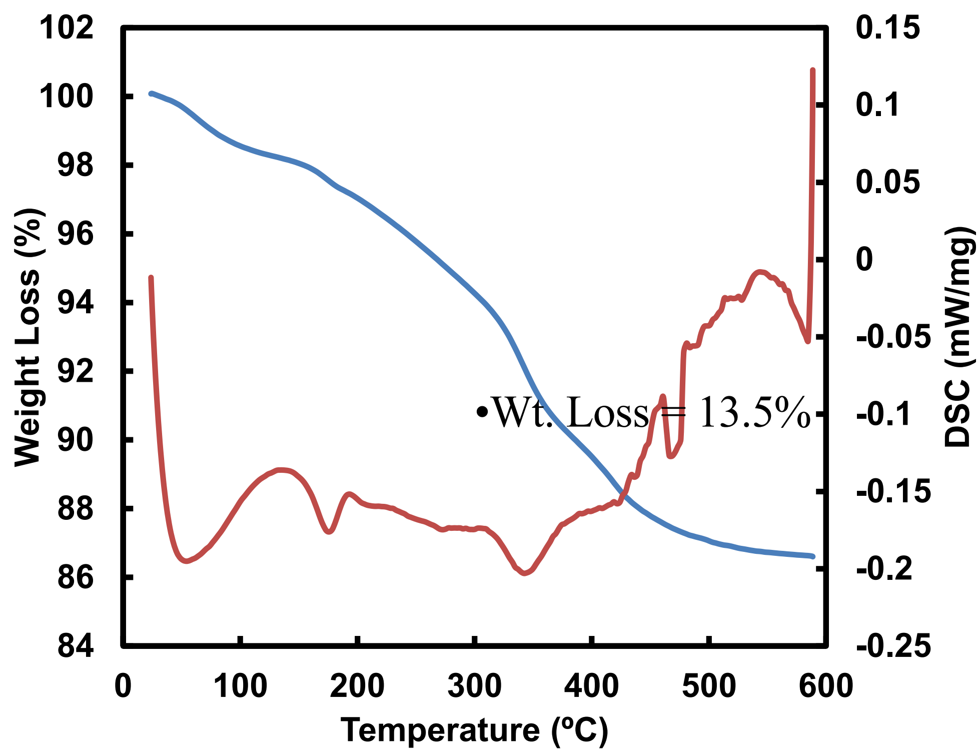
MgO + Molten Salts to enhance capacity/kinetics

•Wt. Loss = 11.5%



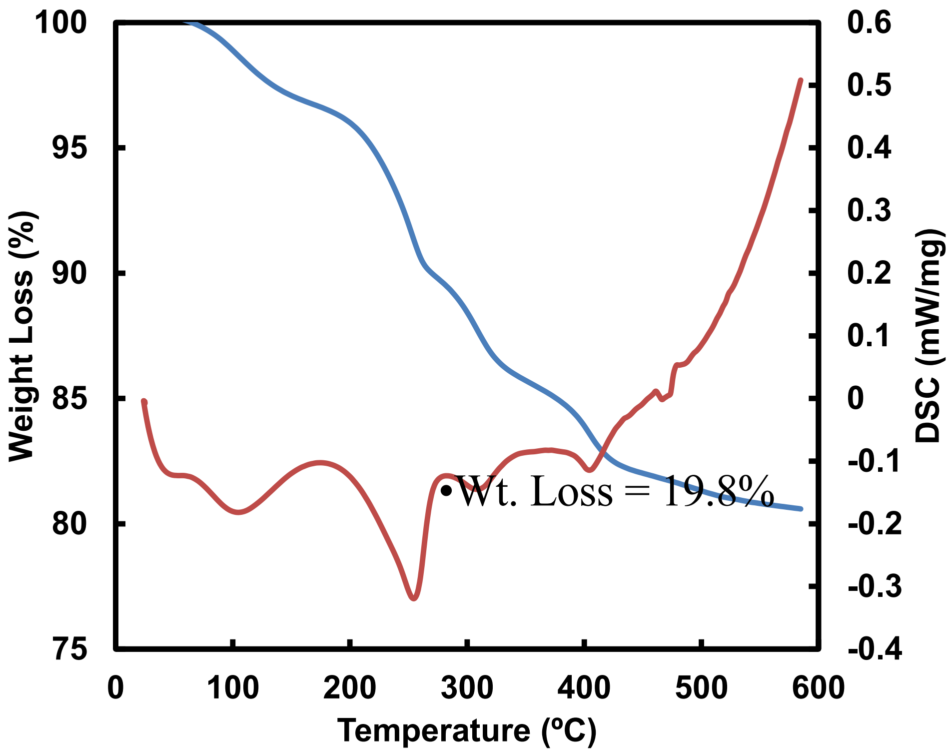
•MgO + LiKNa Acetate



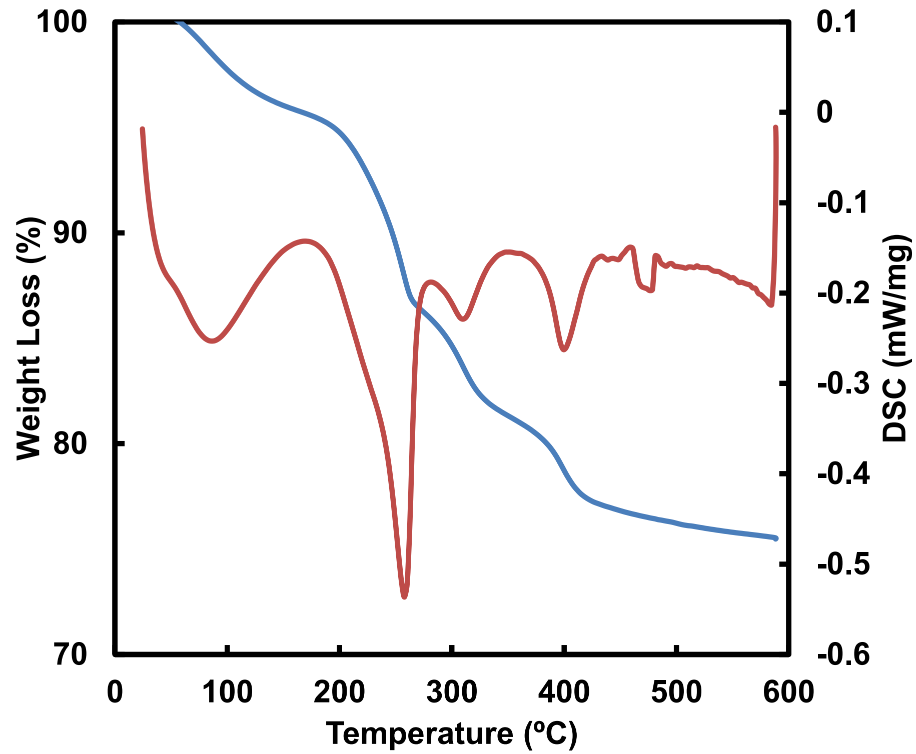
•MgO + LiKNa Acetate + NH_3

MgO + Molten Salts

•MgO + NH_4 Acetate

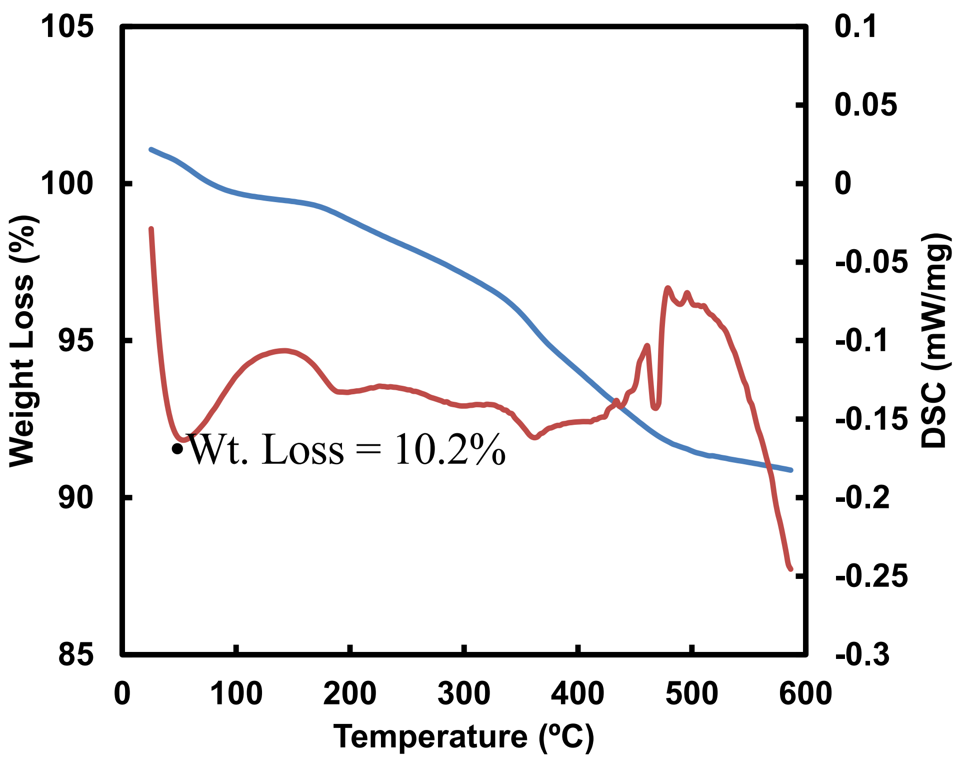


•MgO + NH_4 Acetate + NH_3

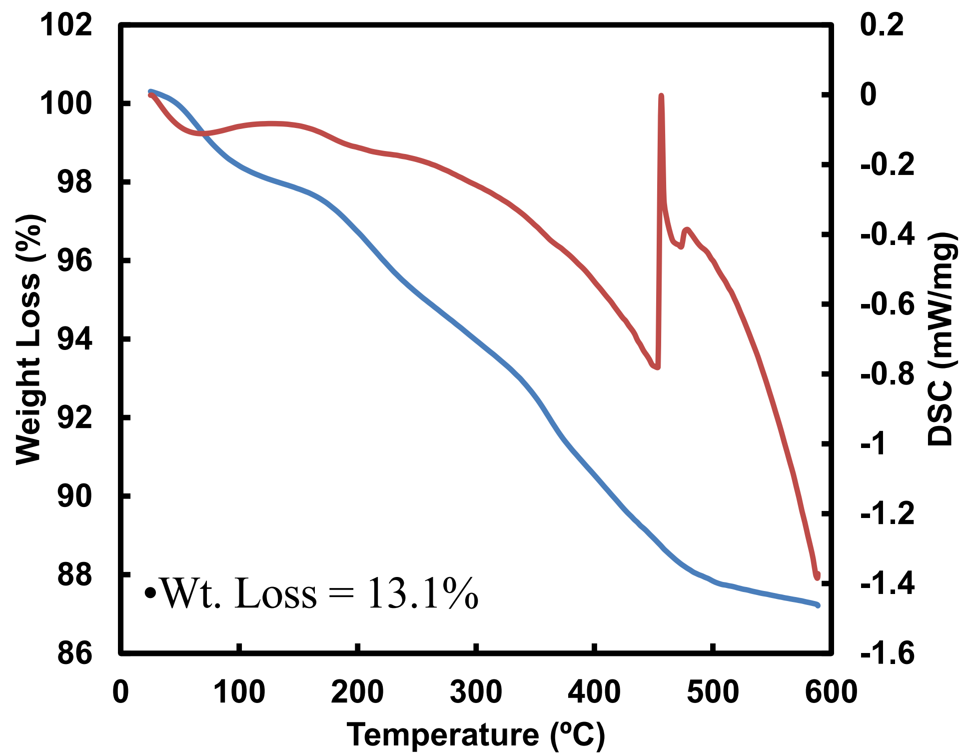


MgO + Molten Salts

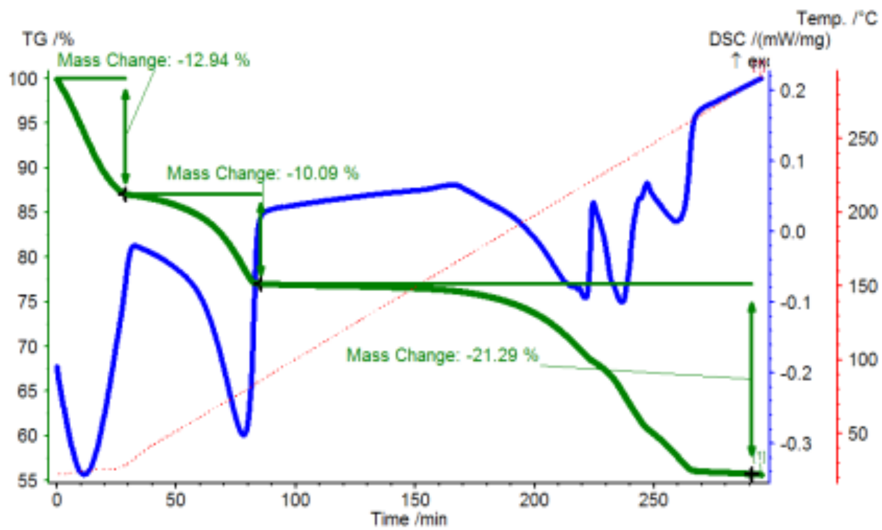
•MgO + CsNa Acetate

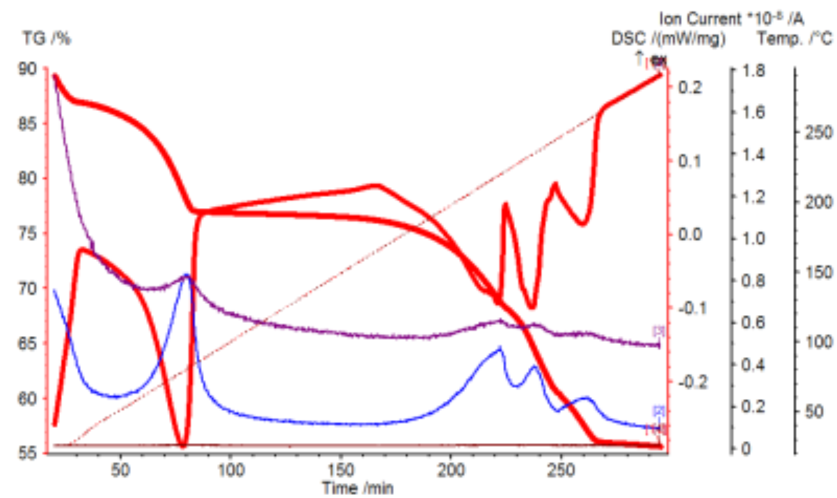


•MgO + CsNa Acetate + NH_3



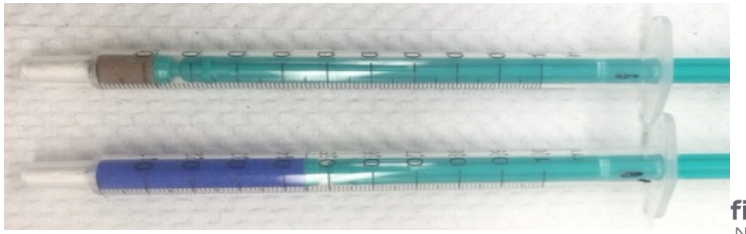
Copper Chloride and Copper Amine Complex





- Weight Loss = 44.32%

- $CuCl_2$
- $Cu(NH_3)_xCl_2$



Metal Ammine Complex NH_3 Capacity

Material	% Weight Loss (TGA)
Mg-Ammine Chloride	51.84
Ca-Ammine Chloride	24.0
Sr-Ammine Chloride	11.9
Li-Ammine Chloride	48.7
Mn-Ammine Chloride	24.0
Co-Ammine Chloride	42.5
Ni-Ammine Chloride	38.6
Cu-Ammine Chloride	44.3

Purpose of Transition metal ammines

a. Tune acidity
b. Tune thermodynamics

Comparison of ammonia capacities of screened metal ammine complexes

Summary

- Completed the synthesis and evaluation of several Eutectic and double salts.
- Characterize and Study the NH_3 uptake capacity of the Eutectic salts.
- Evaluated ammonia storage capacity of oxide based materials
- Underway
  - Acidic oxide materials with and without solid solution
  - Impact of surface area and porosity of oxidic materials ammonia uptake