Next Generation SCR-Dosing System Investigation

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Project Overview

Timeline

- Start – Oct 2014
- End – Sept 18

Budget

- Matched 80/20 by USCAR as per CRADA agreement
- DOE funding for FY16: $200K;

Barriers

Addressed in next slide

Partners

- Pacific Northwest National Laboratory
- USCAR

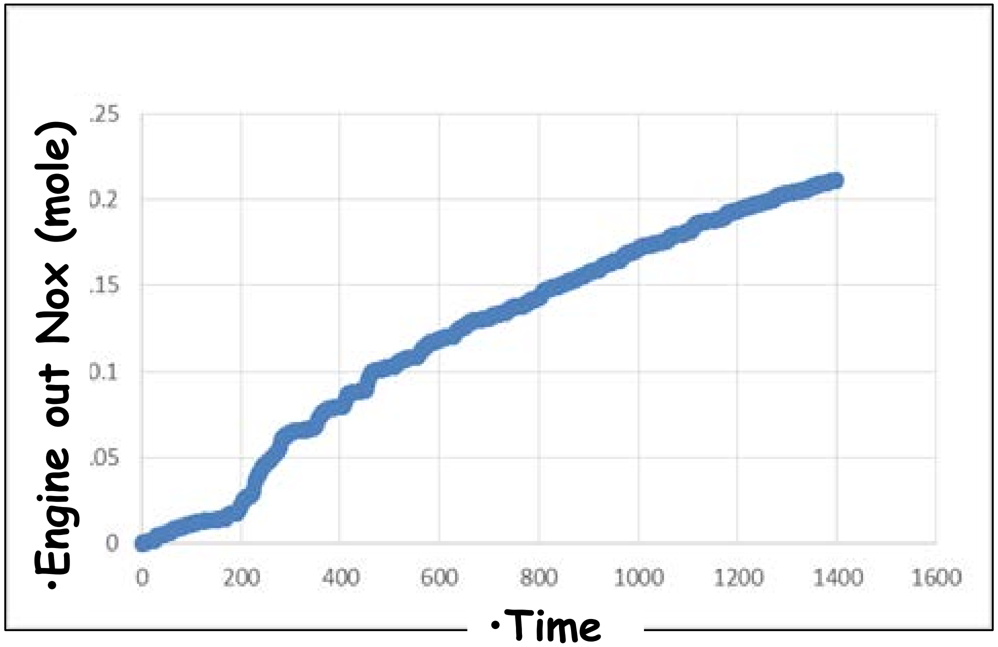
Barriers - Relevance

- 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

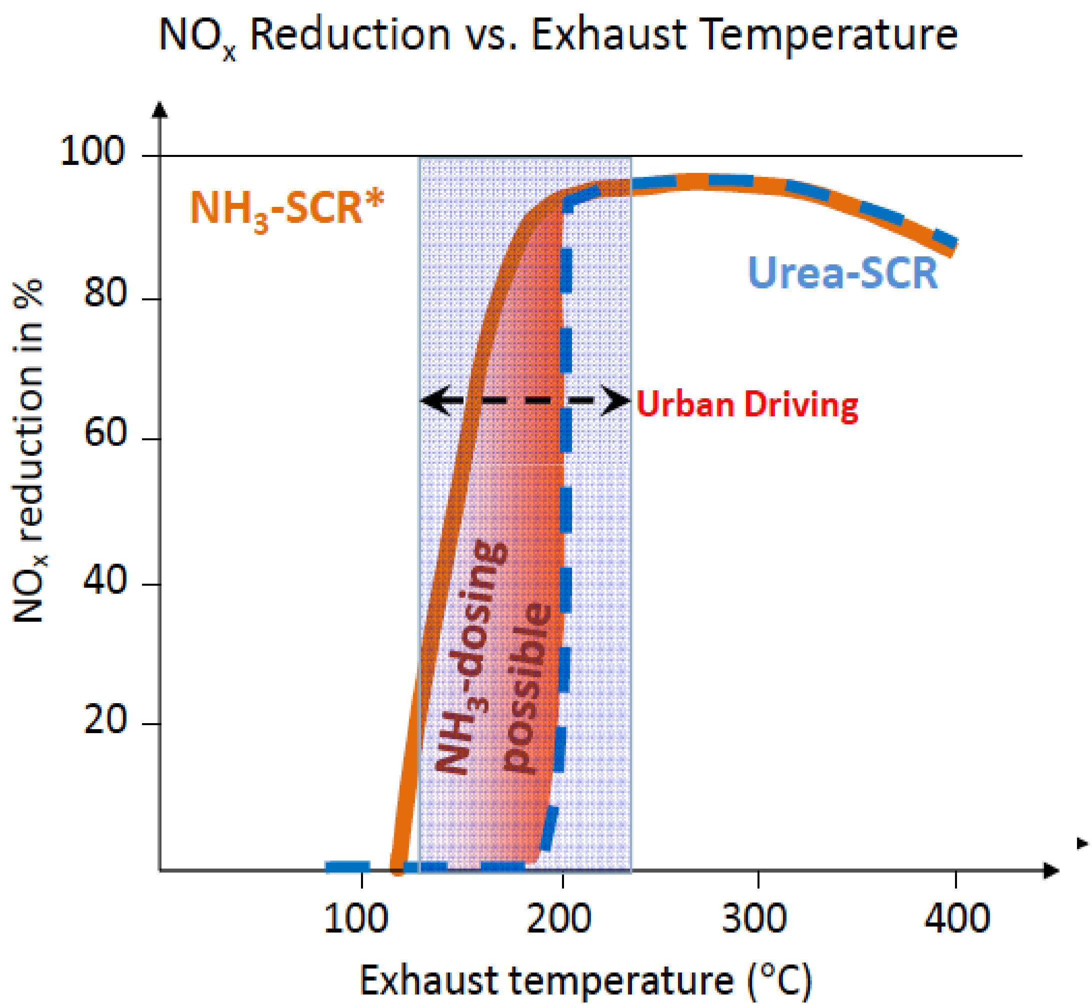


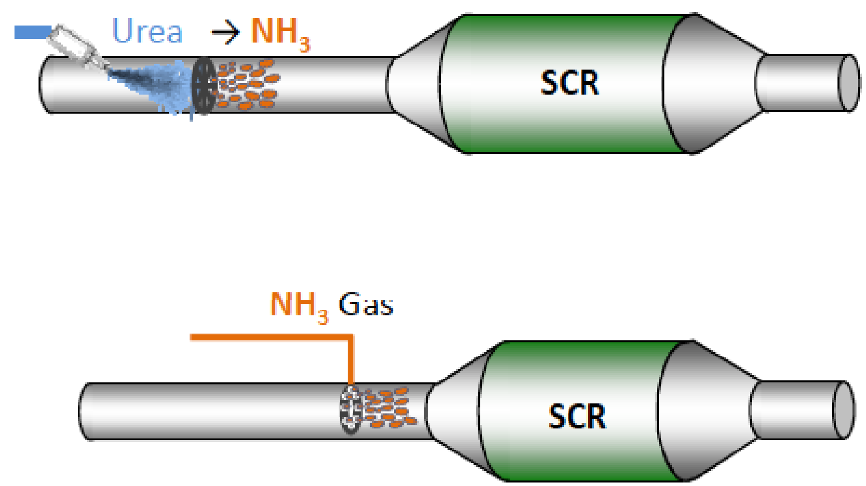
	USCAR FTP cycle
Total NH3	4.8 g
Avg. mass flow	3.1 mg/s
Peal flow	22.6 mg/s
Cycle length	1399 sec

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

Item	Unit	20 ^{o}C	-7 ^{o}C	-15 ^{o}C
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

Direct NH_3 dosing



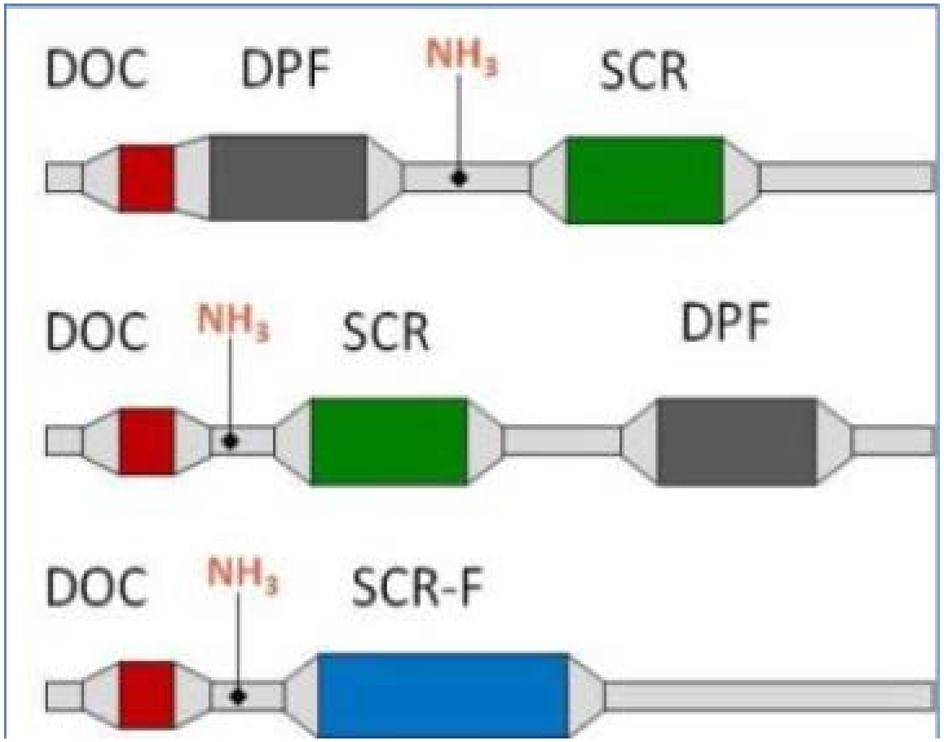


Direct NH_3-dosing enables good SCR performance during urban driving without deposit risk.

* NH_3-SCR efficiency: W. Tang et al. BASF, DOE-DEER conference, October 4th 2011, p.3

Advantages of Direct NH_3 Dosing

- NO x reduction under all conditions
  - – Low/medium engine load; low ambient temperature
  - – Works when the SCR catalyst is active
- Low impact on fuel economy
  - – No need to inject extra fuel for exhaust temperature management
- Easy & flexible exhaust interface
  - – Simple interface & no injector
  - – No risk of deposits
  - – Close-coupled gas/gas mixing possible
- No shelf life issues for NOx reductant
  - – No degradation or freezing; unlimited shelf life



- A flexible and compact exhaust system

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

Vehicle Technologies Office

- 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)

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Reviewer Comments

- Project needs to consider non-chlorine materials that will not produce hydrogen chloride (HCl)
- Expressed a consideration that conference calls every two or three months to be very low collaboration, and suggested it is an industrial's dream.
- Downgrading carbamate as a urea replacement, because it yields CO_2 as a decomposition product, is not appropriate

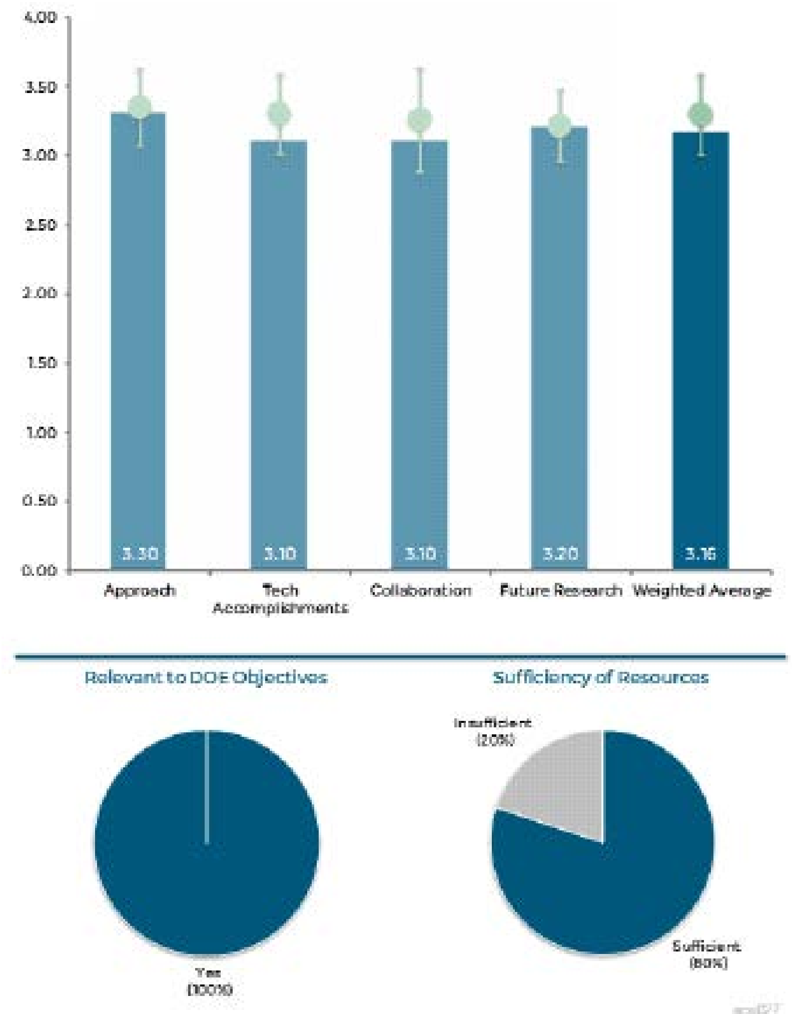

Figure 4-19 Thermally Stable Ultra Low-Temperature Oxidation Catalysts: Abhijeet Karkamkar (Pacific Northwest National Laboratory) - Advanced Combustion Engines

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Response to Reviewer Comments

- HCl: We quantified HCl, developed pathways to mitigate HCl
- Limited communications: We have increased communication with USCAR to address this comment
- Down-selection criterion: Deposition of ammonium carbamate was identified by USCAR as a serious issue

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

DEFBlue™ Vs. $MgCl_2.6NH_3$

DEFBlue™

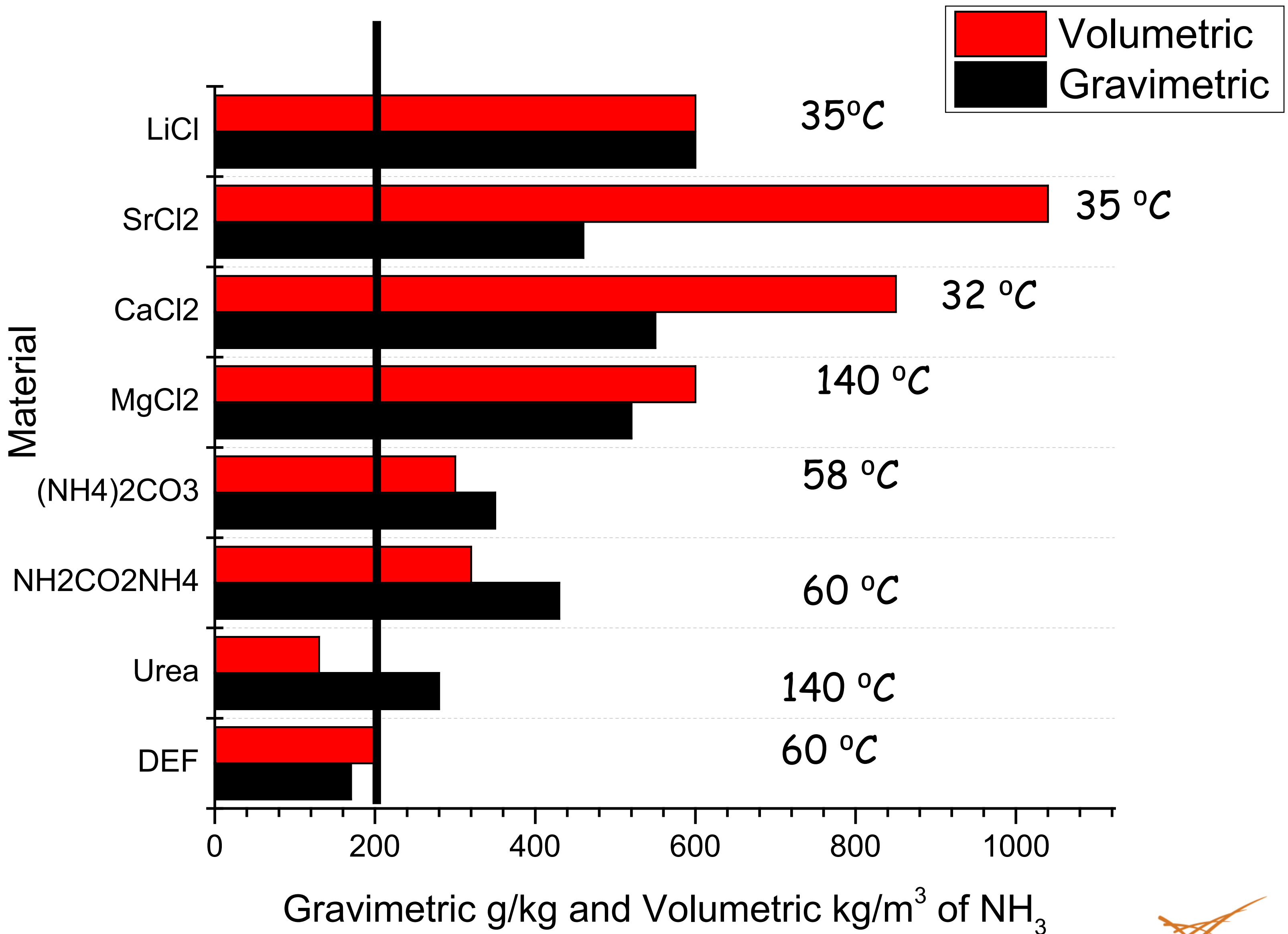
- 30% Urea +70% Water
- 200 kg NH_3/m^3
- 17 wt% NH_3 (on composition basis)
- Convenient
- Freezing
- Solid deposits
- Lowering of exhaust temp due to water

$MgCl_2.6NH_3$

- ~ 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

Summary of material properties



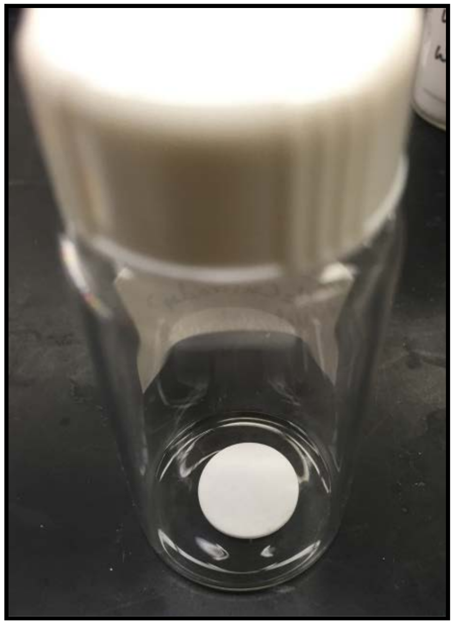
Need for new materials

- Existing materials have limitations
- New materials and composites are needed to address these limitations
- Synthesis of Eutectics and double salts
- Ammonia Absorption into Alkaline Earth Metal Halide Mixtures as an Ammonia Storage Material *Chun Yi Liu and Ken-ichi Aika Ind. Eng. Chem. Res. 2004, 43, 7484-7491*
- Development of new additives to enhance kinetics, thermodynamics and stability
- Ammonia Adsorption on Ion Exchanged Y-zeolites as Ammonia Storage Material *Chun Yi Liu and Ken-ichi Aika Journal of the Japan Petroleum Institute, 46, (5), 301-307 (2003*
- Theory can help identify potential systems
- *Designing mixed metal halide ammines for ammonia storage using density functional theory and genetic algorithms Peter Bjerre Jensen,Steen Lysgaard,Ulrich J. Quaade and Tejs Vegge, Phys.Chem.Chem.Phys.,2014,16, 19732—19740*

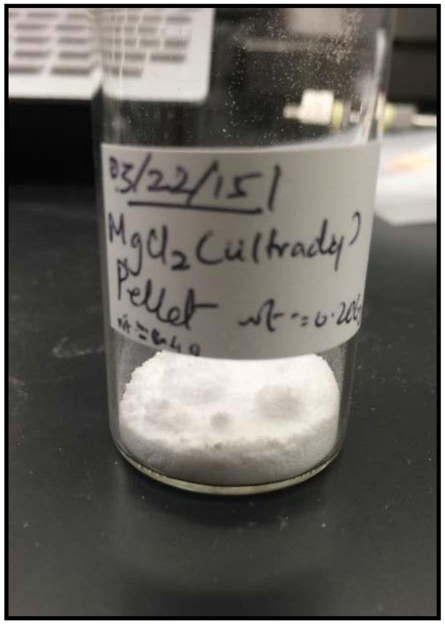
Recent Accomplishments

- Completed the large scale (5-25 g scale) loading of NH_3 on anhydrous .
- Completed the synthesis and evaluation of 10%$NiCl_2$ on $MgCl_2$ and 10%$CoCl_2$ on $MgCl_2$ via aqueous solution method.
- Characterize and Study the NH_3 uptake capacity of the Eutectic salts.
- Quantify and Minimize volume expansion upon NH_3 uptake
- Evaluated ammonia storage capacity of oxide based materials
- Nano-encapsulation studies of $MgCl_2$ in high surface area and porous supports
- Identify and quantify and mitigate HCl being released
- Underway
  - Effect of CO_2 on material performance
  - Kinetics of NH_3 release from composites
  - Effect of NOx, H_2O, CO on material performance

Effect of NH_3 on pellets



- Pellet-$MgCl_2$
- Before NH_3 adsorption
- Wt.=0.205 g
- Dia.= 9 mm
- Height = 0.05 mm

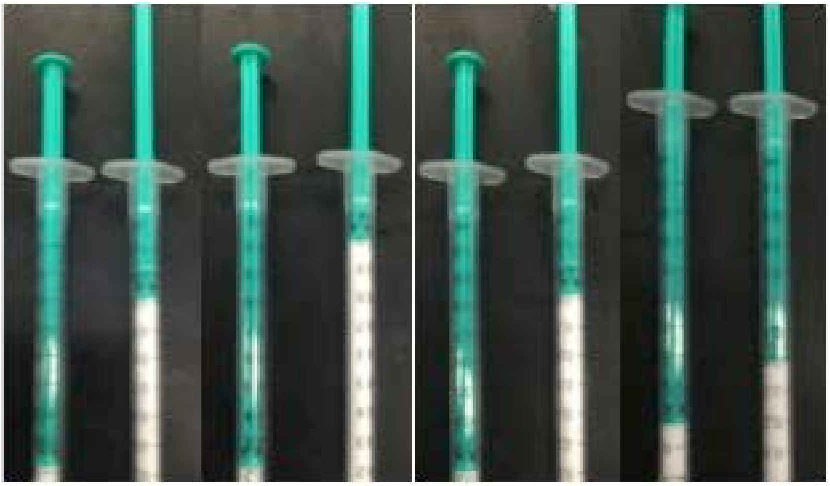


- Pellet-$MgCl_2$
- After NH_3 adsorption
- Wt.=0.4 g

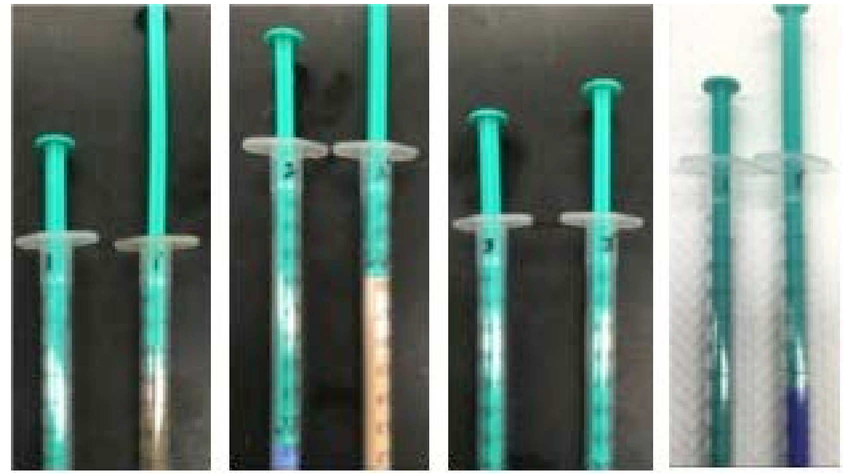
- Loses engineered form ✗
- Only NH_3 released ✓
- > 50 wt% gravimetric capacity ✓
- Reversible ✓

New additives are needed to retain engineered form

Volume Expansion Measurements



$MgCl_2$ $CaCl_2$ $SrCl_2$ LiCl



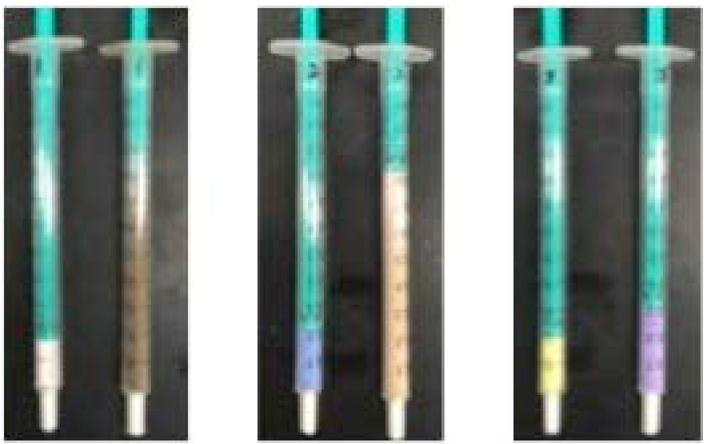
$MnCl_2$ $CoCl_2$ $NiCl_2$ $CuCl_2$

Material	Weight (g)	Volume (cc)	Density (g/cc)	Volume change (%)
$MgCl_2$	0.200	0.22	0.91	-
$Mg(NH_3)_6Cl_2$	0.3622	0.80	0.45	**264**
$CaCl_2$	0.202	0.22	0.92	-
$Ca(NH_3)_8Cl_2$	0.4212	1.00	0.42	**354**
$SrCl_2$	0.203	0.22	0.92	-
$Sr(NH_3)_8Cl_2$	0.3697	0.80	0.46	**264**
LiCl	0.200	0.18	1.11	-
$Li(NH_3)_xCl$	0.3212	0.40	0.80	**122**

Material	Weight (g)	Volume (cc)	Density (g/cc)	Volume change (%)
$MnCl_2$	0.202	0.17	1.19	-
$Mn(NH_3)_6Cl_2$	0.346	0.80	0.43	**370**
$CoCl_2$	0.205	0.20	1.02	-
$Co(NH_3)_6Cl_2$	0.355	0.80	0.44	**300**
$NiCl_2$	0.200	0.20	1.00	-
$Ni(NH_3)xCl_2$	0.314	0.30	1.05	**50**
$CuCl_2$	0.200	0.11	1.82	-
$Cu(NH_3)_xCl_2$	0.322	0.45	0.72	**310**

Large volume expansion upon addition of NH_3 is a big problem

Transition metal ammine complexes



$MnCl_2$ $CoCl_2$ $NiCl_2$

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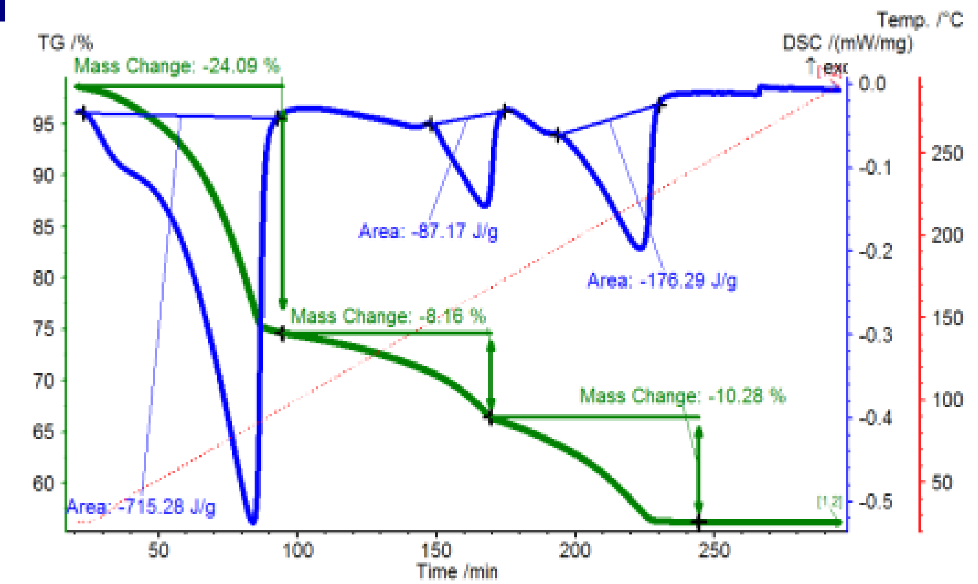
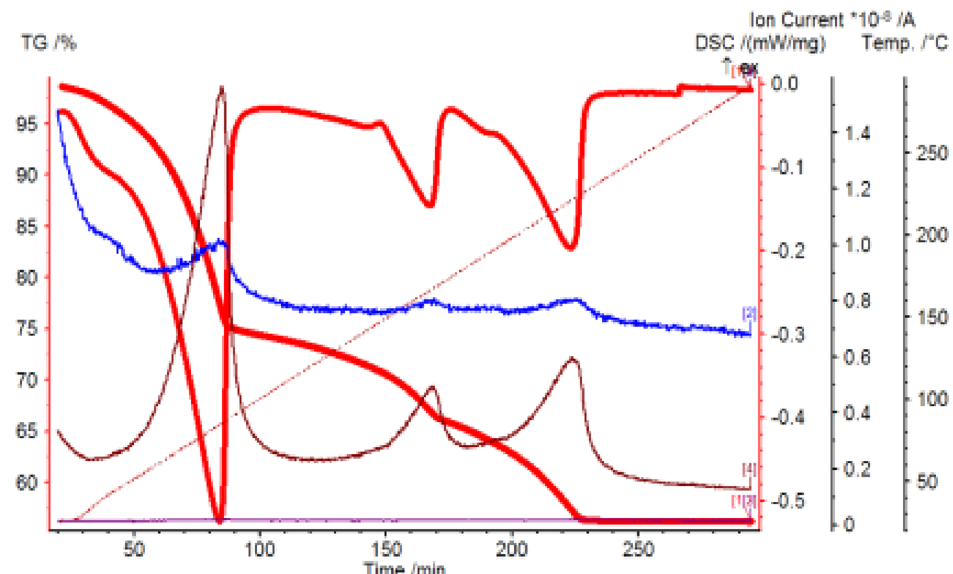
$MnCl_2$	0.202	0.17	1.19
$Mn(NH_3)_6Cl_2$	0.346	0.80	0.43
$CoCl_2$	0.205	0.20	1.02
$Co(NH_3)_6Cl_2$	0.355	0.80	0.44
$NiCl_2$	0.200	0.20	1.00
$Ni(NH_3)xCl_2$	0.314	0.30	1.05





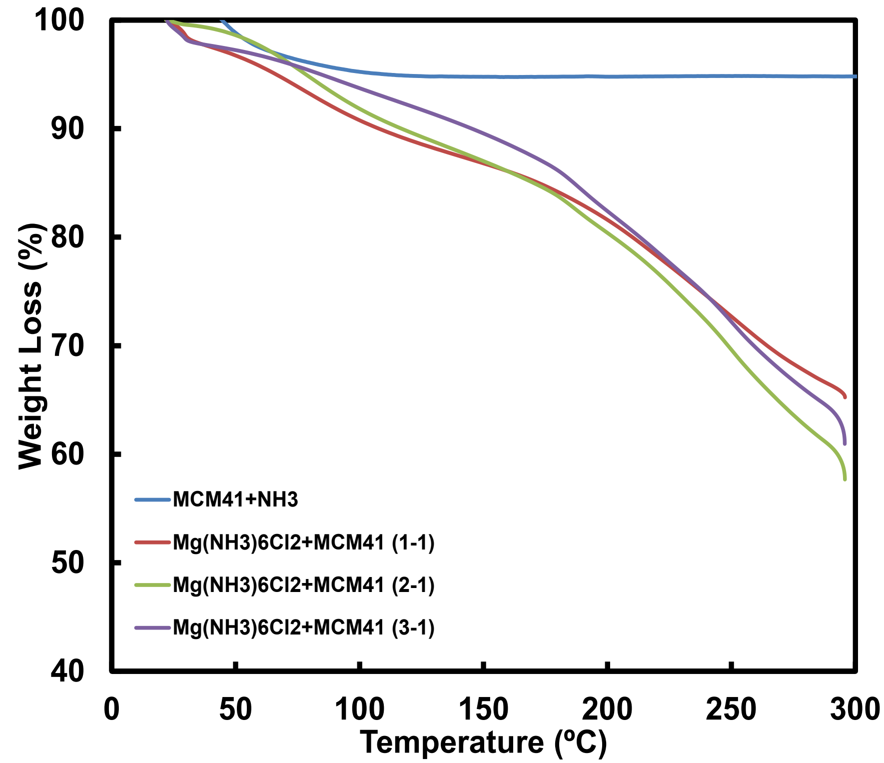
Transition metal ammines provide a pathway to tune acidity hence tune thermodynamics

- **Weight Loss =42.5%**
- $Co(NH_3)_6Cl_2$

High Surface Area Supports:MCM-41

1:1 2:1 3:1

1:1 2:1 3:1



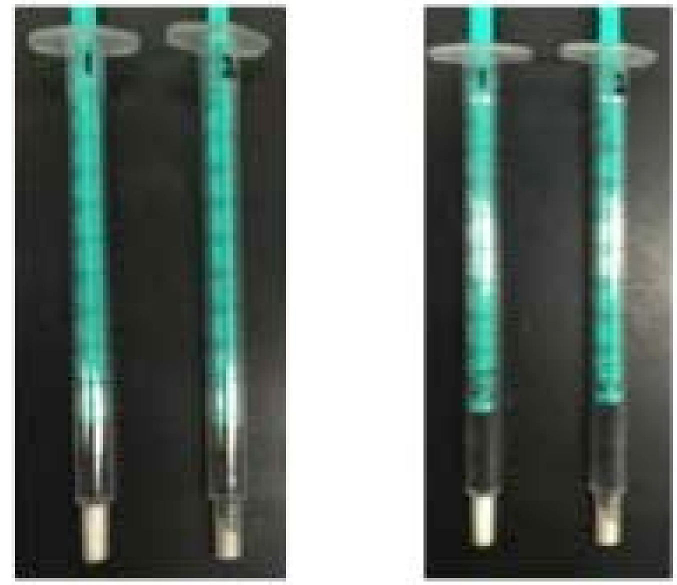
Material	Weight (g)	Volume (cc)	Density (g/cc)	Volume Change (%)
$MgCl_2$:MCM41 (1:1)	0.207	0.42	0.49	-
$Mg(NH_3)_6Cl_2$:MCM41 (1:1)	0.265	0.49	0.54	16.7
$MgCl_2$:MCM41 (2:1)	0.200	0.34	0.59	-
$Mg(NH_3)_6Cl_2$:MCM41 (2:1)	0.28	0.44	0.64	29.4
$MgCl_2$:MCM41 (3:1)	0.15	0.25	0.60	-
$Mg(NH_3)_6Cl_2$:MCM41 (3:1)	0.22	0.33	0.67	32.0

- $MgCl_2$ was impregnated on the high surface area MCM-41.
- Higher amounts of $MgCl_2$ loading does not improve the NH_3 capacity.
- **MCM41 support provides relatively better mechanical stability.**

Activated Carbon as nano-encapsulation material

Material	Surface Area (m^2/g)	Pore Volume (cc/g)
Activated Carbon	450.1	1.31
AC:$MgCl_2$ (1:1)	107.7	0.35
AC:$MgCl_2$ (1:2)	81	0.33
AC:$MgCl_2$ (1:3)	97.3	0.38
AC-KB-B100	1321	1.38
$MgCl_2$:AC (1:1)	140.7	0.20
$MgCl_2$:AC (2:1)	81.5	0.14
$MgCl_2$:AC (3:1)	164.5	0.32

AC:$MgCl_2$ AC:$Mg(NH3)_6Cl_2$



1:1 1:2 1:1 1:2

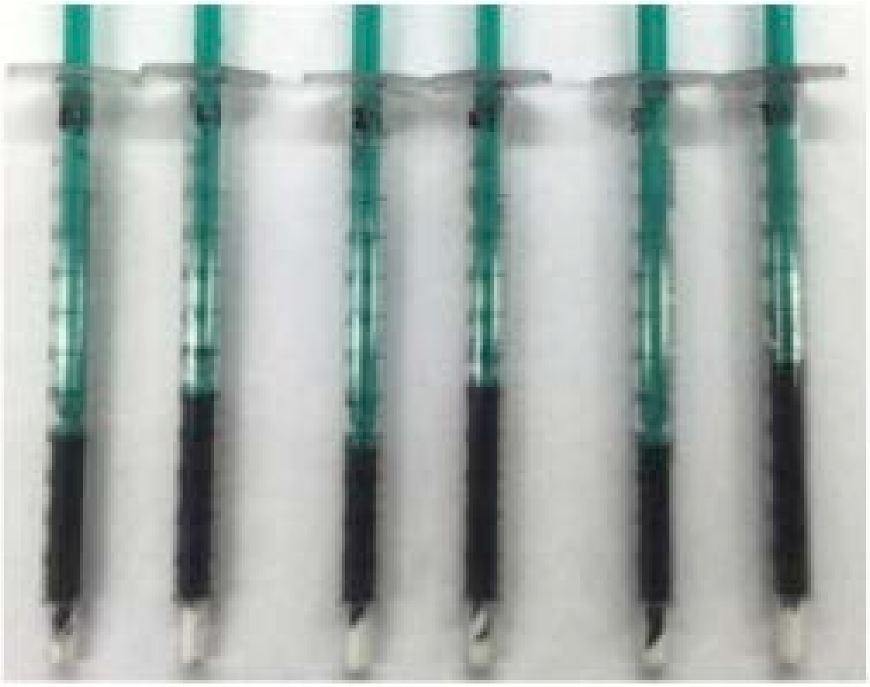
Material	Weight (g)	Volume (cc)	Density (g/cc)
AC:$MgCl_2$ 1:1	0.104	0.18	0.58
AC:$Mg(NH_3)_6Cl_2$ 1:1	0.142	0.23	0.62
AC:$MgCl_2$ 1:2	0.104	0.17	0.61
AC:$Mg(NH_3)_6Cl_2$ 1:2	0.151	0.25	0.60

Developed an optimized method of incorporation of $MgCl_2$ in porous, high surface area materials

High Surface Area Supports: Activated Carbon

Material	Surface Area (m^2/g)	Pore Volume (cc/g)
Activated Carbon	450.1	1.31
AC:$MgCl_2$ (1:1)	107.7	0.35
AC:$MgCl_2$ (1:2)	81	0.33
AC:$MgCl_2$ (1:3)	97.3	0.38

Material	Weight (g)	Volume (cc)	Density (g/cc)	Volume Change (%)
AC:$MgCl_2$ 1:1	0.15	0.38	0.39	-
AC:$Mg(NH_3)_6Cl_2$ 1:1	0.19	0.49	0.39	**28.9**
AC:$MgCl_2$ 1:2	0.15	0.38	0.39	-
AC:$Mg(NH_3)_6Cl_2$ 1:2	0.20	0.51	0.39	**34.2**
AC:$MgCl_2$ 1:3	0.15	0.38	0.39	-
AC:$Mg(NH_3)_6Cl_2$ 1:3	0.22	0.58	0.38	**52.6**

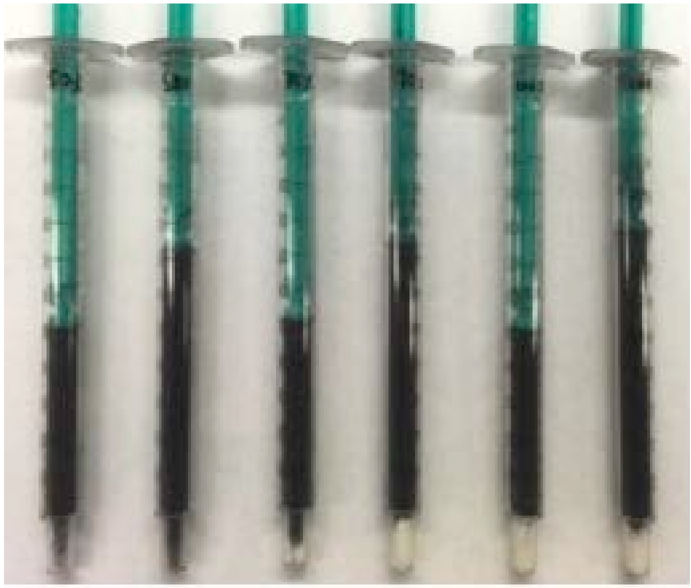


1:1 2:1 3:1

Volume expansion minimized with minimal loss of NH_3 storage capacity

High Surface Area Supports: KBB-100

Material	Surface Area (m^2/g)	Pore Volume (cc/g)
KBB-100	1321	1.38
$MgCl_2$:KBB100 (50%)	140.7	0.20
$MgCl_2$:KBB100 (70%)	81.5	0.14
$MgCl_2$:KBB100 (100%)	164.5	0.32



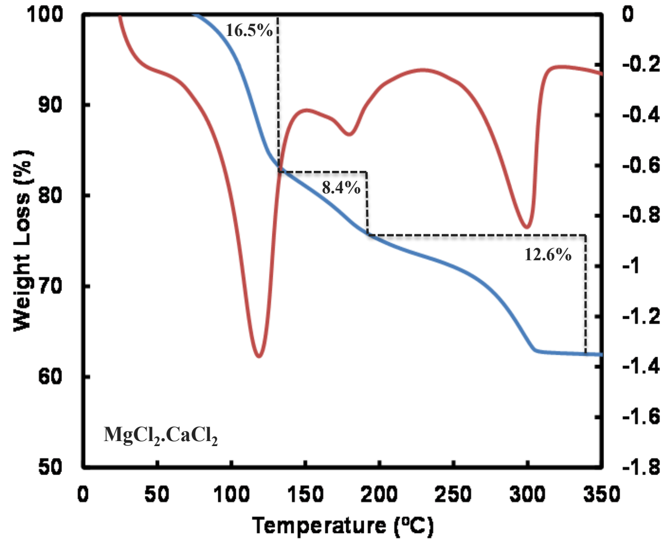
1:1 2:1 3:1

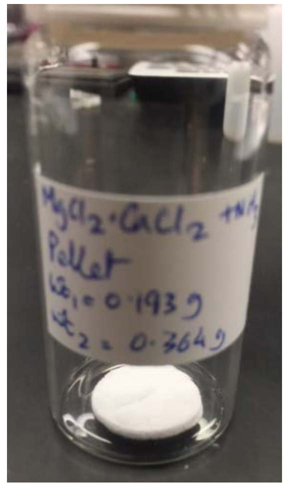
Material	Weight (g)	Volume (cc)	Density (g/cc)	Volume Change (%)
$MgCl_2$-KBB100 (50%)	0.20	0.50	0.40	-
$Mg(NH_3)_6Cl_2$-KBB100 (50%)	0.24	0.71	0.34	**42.0**
$MgCl_2$-KBB100 (70%)	0.20	0.50	0.40	-
$Mg(NH_3)_6Cl_2$-KBB100 (70%)	0.27	0.72	0.37	**44.0**
$MgCl_2$-KBB100 (100%)	0.20	0.50	0.40	-
$Mg(NH_3)_6Cl_2$-KBB100 (100%)	0.30	0.80	0.37	**60.0**

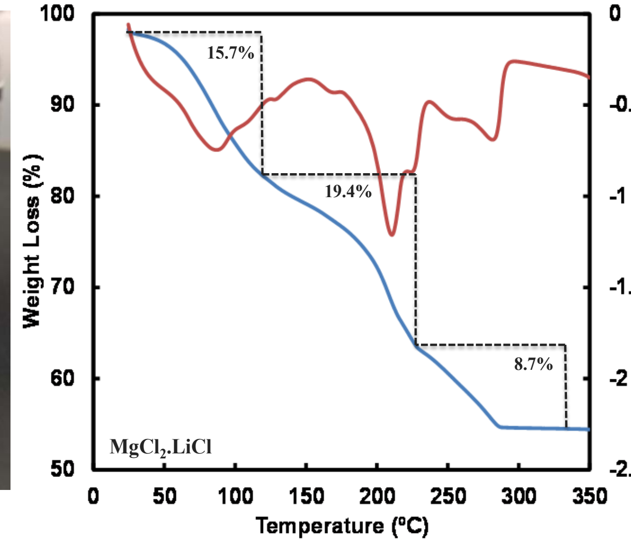
Volume expansion minimized with minimal loss of NH_3 storage capacity

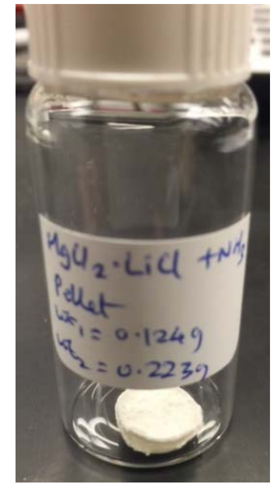
NH_3 Storage on Double Salts

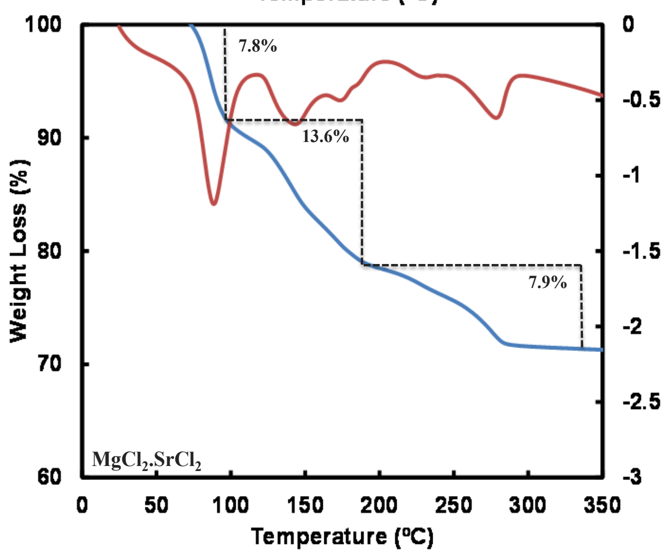
Vehicle Technologies Office

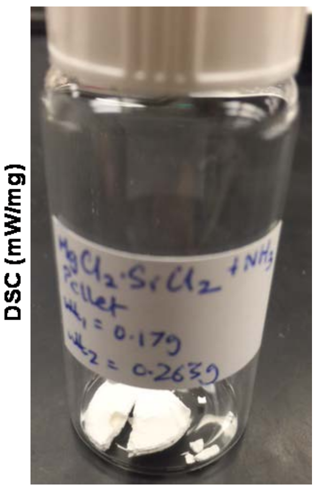


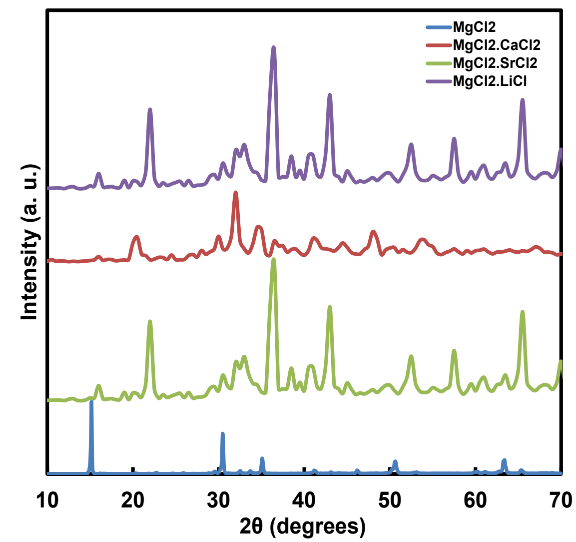










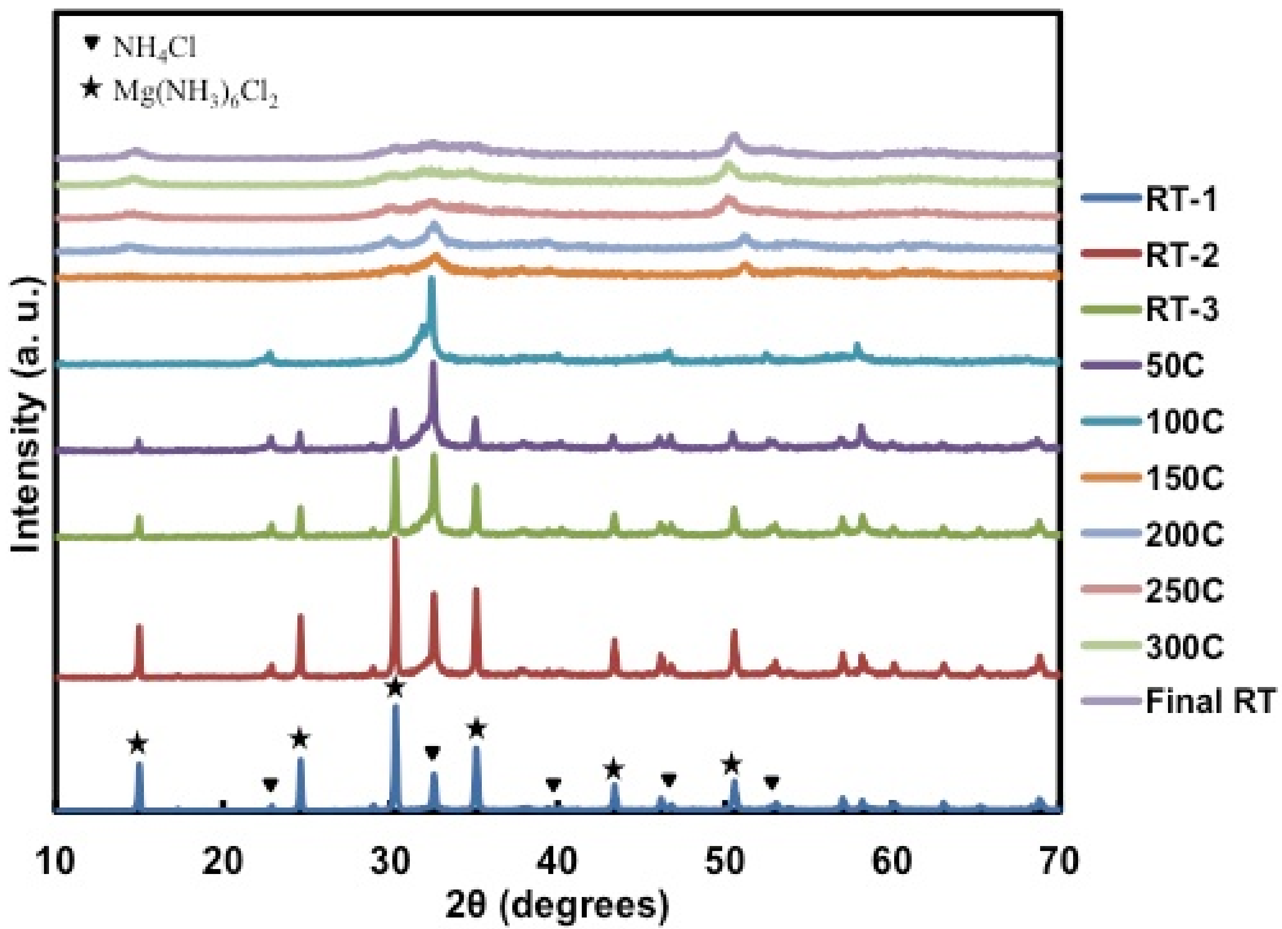


The Mechanical stability of the double salt is better in comparison to $MgCl_2$.

The NH_3 capacity of these double salts is comparable to Magnesium Ammine Chloride.

High Temperature Powder XRD Patterns: Mg-Ammine Complex

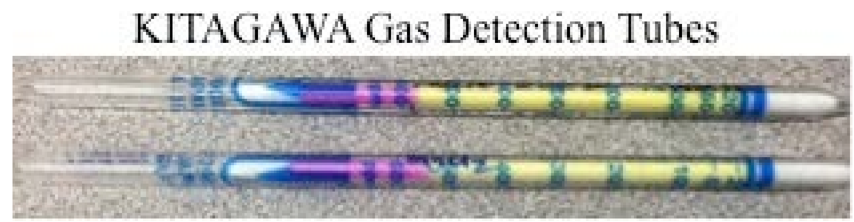
Vehicle Technologies Office



- The powder XRD pattern reveals that we have a mixture of Mg-ammine complex and ammonium chloride.
- The decomposition of the ammine complex starts at room temperature due to the release of physisorbed ammonia.
- As the temperature is increased we observe complete release of ammonia and after 300°C we are left with amorphous material..

Impurity Quantification and Mitigation: HCl Measurements

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



Successful mitigation of HCl by development of composites

Summary

Vehicle Technologies Office

- Completed the synthesis and evaluation of several Eutectic and double salts.
- Characterize and Study the NH_3 uptake capacity of the Eutectic salts.
- Quantified and Minimized volume expansion upon NH_3 uptake (from 300% to 30%)
- Evaluated ammonia storage capacity of oxide based materials
- Nano-encapsulation studies of $MgCl_2$ in high surface area and porous supports for mitigation of volume expansion and HCl formation
- Identify, quantify and mitigate impurities. (HCl >600 ppm to <1 ppm)
- Underway
  - Effect of CO_2 on material performance
  - Kinetics of NH_3 release from composites
  - Effect of NOx, H_2O, CO on material performance

Planned Future Work

1. **Composites, Double Salts and Eutectics:** Studies will be especially focused on mechanisms/limitations for low temperature performance. Some specific questions:
   - How will additives alter capacity?
   - Gravimetric and volumetric
   - How will additives impact thermodynamics and kinetics? Energy requirements and HCl
   - How additives help retain engineered form?

• HCl

2. **NH_3 Adsorption Materials:**
   - Finish stability testing of existing materials
   - Pathways to mitigate HCl (Oxide materials)
3. **Material Cost analysis**