A Study on Synthetic Method and Material Characteristics of Metal Ammine Chlorides as Ammonium Transport Materials for Solid SCR

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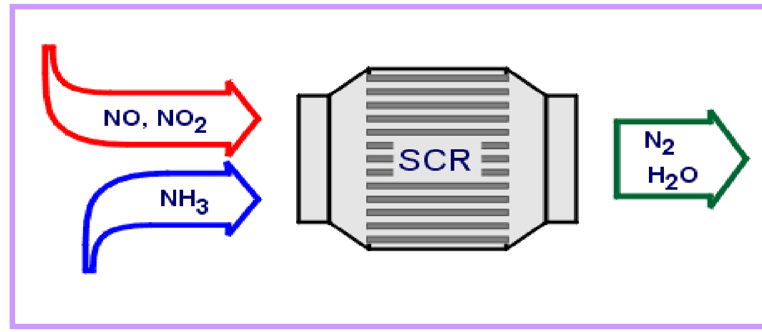
2016 DOE CLEERS Workshop
Holiday Inn Ann Arbor, Ann Arbor, MI, USA

Outline

- Introduction of Solid SCR System
- Metal Ammines
- Lab-Scale Experimental Set-Up
- Test Procedure
- Calcium Ammine Chloride (Test Conditions, Density, IC, Simple Weight Calculation, FT-IR, XRD, TGA)
- Magnesium Ammine Chloride (Test Conditions, Density, IC, Simple Weight Calculation, FT-IR, XRD, TGA)
- New Test Procedure for Water Removal
- Concluding Remarks
- Acknowledgement
- Reference

Solid SCR System

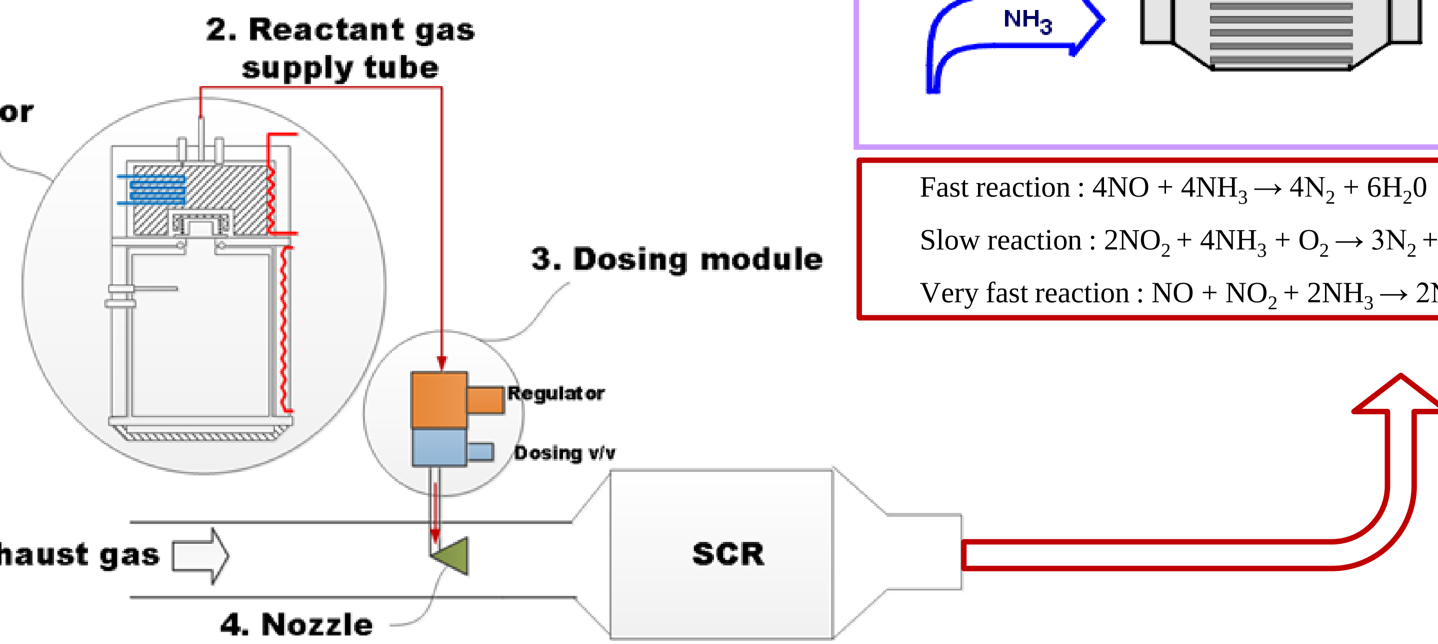
- NOx reduction technology by using NH_3 as a reductant, which is generated from solid ammonium transport materials.



Fast reaction : $4NO + 4NH_3 \rightarrow 4N_2 + 6H_20$

Slow reaction : $2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$

Very fast reaction : $NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$



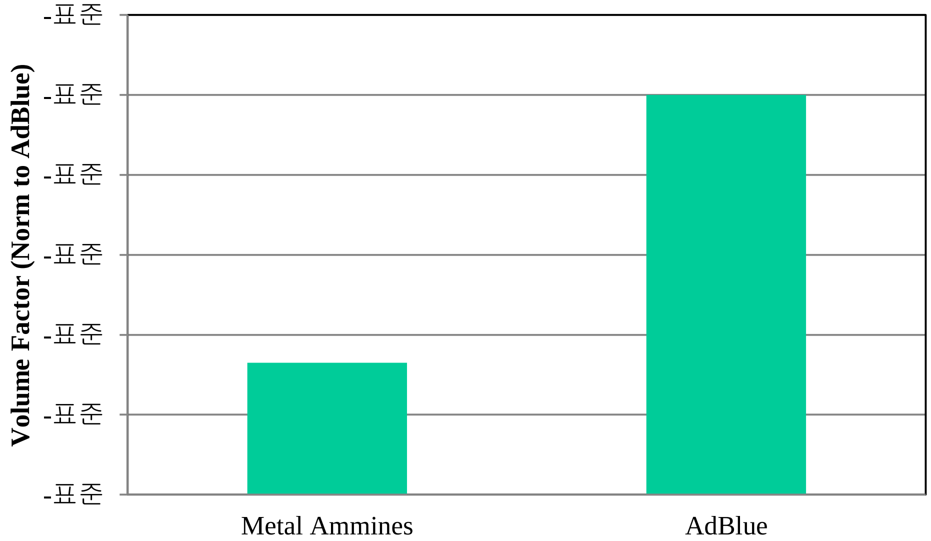
Solid Based SCR

Ammonium Transport Materials	Company	Decomposition Temperature (C)
Solid Urea	Pierburg	140
Ammonia Carbamate	FEV + Tenneco	60
Metal Amine*	Amminex	32~35

(* Calcium Ammine Chloride, Strontium Ammine Chloride)

Advantage
(Compared with Liquid Urea SCR)

- ~3 times of **ammonia storage capacity**
- Improvement of **low temperature** NOx conversion **performance** due to direct ammonia gas injection
- Enhancement of the reactants **mixing characteristics with exhaust gas**



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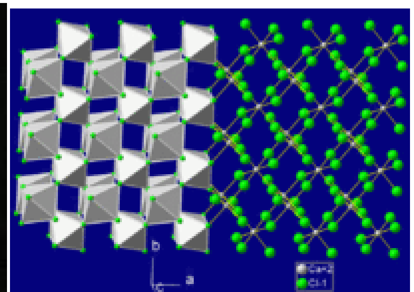
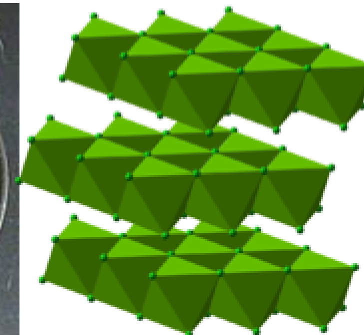
Metal Chlorides

- Calcium Chloride($CaCl_2$)



- Magnesium Chloride($MgCl_2$)



- Strontium Chloride($SrCl_2$)

Material Properties of Metal Ammines

Metal Ammines (Amminex)	Molecular Formula	Molecular Weight g/mol	Density (g/cm^3)	Mols NH_3 per Mol	Volume Factor (Norm to AdBlue®)	Decomp. Temp, °C	NH3 release energy, kJ/mol NH3
Magnesium Chloride	$MgCl_2$	95.21	2.32	0	-	-	-
Magnesium Ammine Chloride	$Mg(NH_3)_6Cl_2$	197.39	1.16	6	0.33	142	87
Calcium Chloride	$CaCl_2$	110.99	2.15	0	-	-	-
Calcium Ammine Chloride	$Ca(NH_3)_8Cl_2$	247.23	1.09	8	0.33	32	69
Strontium Chloride	$SrCl_2$	158.53	3.052	0	-	-	-
Strontium Ammine Chloride	$Sr(NH_3)_8Cl_2$	294.77	1.3	8	0.33	35	48

[Ref]

1. G. Fuks et al. "A Review of Solid Materials as Alternative Ammonia Sources for Lean NOx Reduction with SCR", SAE 2009-01-0907
2. Gmelins Handbook 1939, The Hydrogen Fuel Alternative - $MgCl_2$
3. L.J. Gillespie, H.T. Gerry, "Densities, and partial molar volumes of ammonia, for the ammines of calcium and barium chlorides", J. Am. Chem. Soc. , 1931, 53(11), pp. 3962-3968 - $CaCl_2$
4. EP 2428490A1 - $SrCl_2$

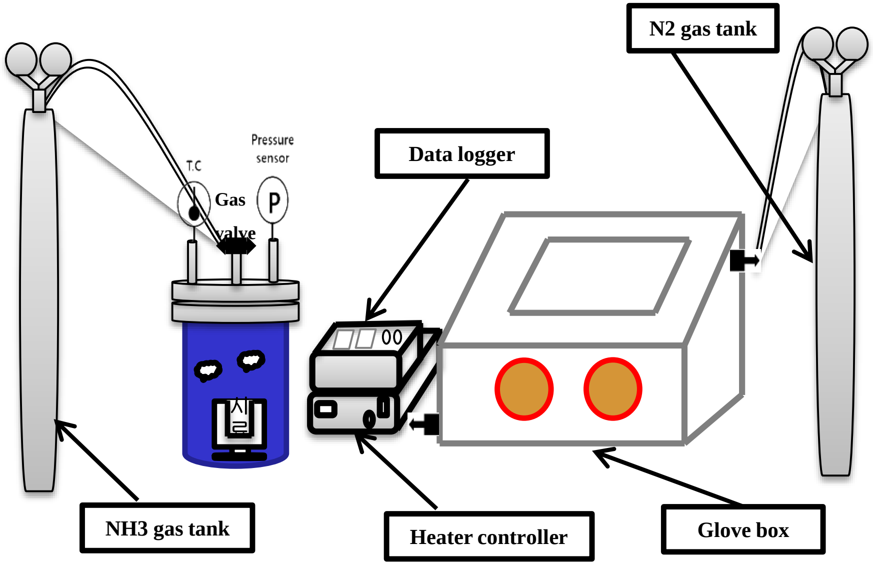
Supply Information of Metal Chlorides

Material	Form	Supplier	Safety	Cost	Note	Picture
Magnesium Chloride ($MgCl_2$)	Odorless white crystals	Sigma Aldrich	No possibility of hazardous reactions	\$320 / 1 kg (₩371,000)	anhydrous ≥99.0%	
Calcium Chloride ($CaCl_2$)	Odorless white crystals	Sigma Aldrich	No possibility of hazardous reactions	\$360 / 500 g (₩422,000)	anhydrous ≥98.0%	
Strontium Chloride ($SrCl_2$)	Odorless white crystals	Alfa Aesar	Skin irritation and respiratory disease caused by inhalation of dust	\$260 / 100 g (₩300,000)	anhydrous ≥99.5%	

1. Strontium Chloride : anhydrous 99.5%, Green Stone Swiss Co. Limited, \$600 / 500 g (₩700,000)
2. Varied price depends on purity and amount of sample

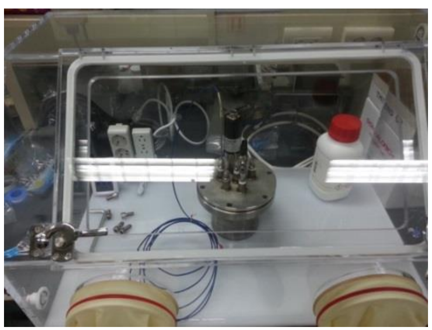
Lab-Scale Experimental Set-Up

- Study synthetic method of metal ammine chlorides ($CaCl_2$, $MgCl_2$ + NH_3 adsorption)
- Simple reactor and glove box was designed and built with ammonia gas tank, nitrogen gas tank, regulator, and DAQ with temperature and pressure sensors.



Test Procedure

- Put a reactor in the glove box, then purge with N_2 gas, in order to remove water content of air.
- Insert metal chloride sample into a reactor and close it in the glove box.
- After take a reactor out of glove box, connect one end of three-way valve with ammonia gas bombe by flexible Teflon tube.
- Adjust temperature of a reactor which is wrap up with heater jacket by heater controller
- Control pressure by a regulator connected to ammonia gas bombe.



Analytical Instruments for Characterization Study

Analytical instruments	Model	Accuracy range
DA	Accupyc 130 pycnometer	20% R.H.
IC	833 Basic IC plus	Velocity of flow : 0.9 mL/min
FT-IR	JASCO FT-IR 4100	Range : 500 ~ 4000 cm-1
XRD	D8 Advance	Range : 10° ~ 90° Step size : 0.02°
SDT(TGA-DSC)	SDT Q600	RT ~ 300° 1°C/min

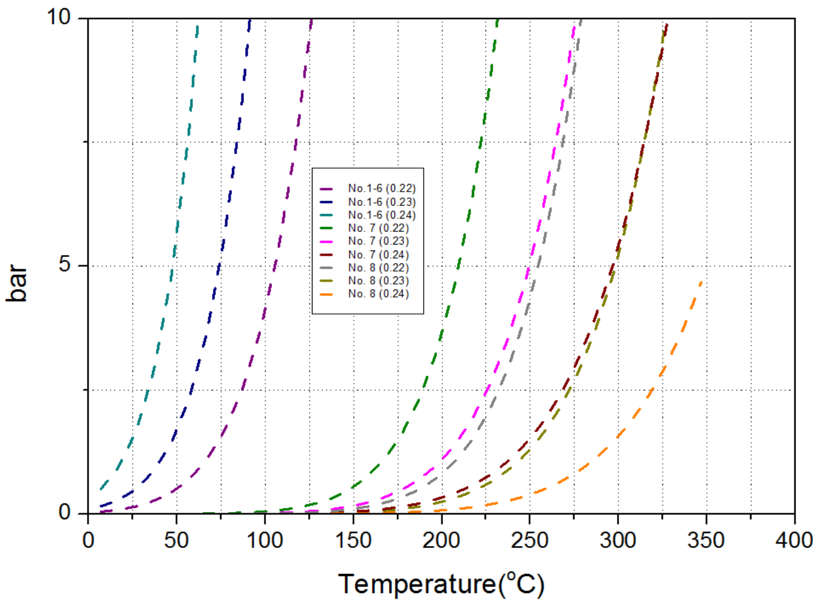
Calcium Ammine Chloride

Desorption Chemistry

$$Ca(NH_3)_8Cl_2 \leftrightarrow Ca(NH_3)_2Cl_2 + 6NH_3 \quad (1)$$

$$Ca(NH_3)_2Cl_2 \leftrightarrow Ca(NH_3)Cl_2 + NH_3 \quad (2)$$

$$Ca(NH_3)Cl_2 \leftrightarrow CaCl_2 + NH_3 \quad (3)$$



Equilibrium vapor pressure of NH_3 from charged $CaCl_2$.

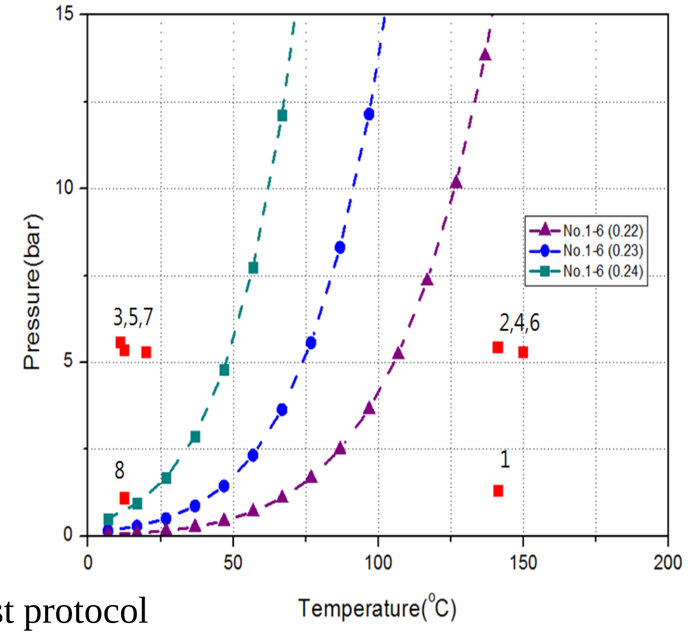
- Equilibrium Vapor Pressure Theory

$$\mathrm{Ln}\,P_{NH3} = \frac{-\Delta_{f,i}}{RT} + \frac{\Delta S_{f,i}}{R} \quad (1)$$

$$P_{NH3(T)} = \exp\left(\frac{-\Delta H_{f,i}}{RT} + \frac{\Delta S_{f,i}}{R}\right) \quad (2)$$

	NH_3 pressure at 25 °C	Desorption enthalpy	Desorption entropy
	bar	kJ/mol	kJ/(mol·K)
$Ca(NH_3)_8Cl_2$	0.63		
No. 1-6		42	0.22-0.24
No. 7		63.2	0.22-0.24
No. 8		69.1	0.22-0.24

Test Conditions of $CaCl_2+NH_3$



- Test protocol

C-1 : $CaCl_2$ + (NH_3)			
Condition	Temperature (°C)	Pressure (bar)	Time (h)
1	141.3	1.306	0
2	140.8	5.444	0.4
3	20	5.306	0.9
4	141.3	5.449	1st day –soaking
5	12.4	5.353	0.67
6	149.9	5.304	2nd day-soaking
7	11.1	5.593	0.67
8	12.4	1.102	3rd day-soaking-end

- Adsorption weight and adsorption rate calculation

C-1 $CaCl_2$ + NH_3			
		Weight(g)	Remarks
m0	Reactor	5953.63	
m1	Initial sample	40.48	
m2(=m0+m1)	Reactor + Initial sample	5994.11	
m3	Reactor + Initial sample + Adsorption capacity	6052.97	1st day
		6054.75	2nd day
		6061.60	3rd day
Δm(=m3-m2)	Adsorption capacity	58.86	1st day
		60.64	2nd day
		67.49	3rd day
Material	Test time	Adsorption rate(%)	Remarks
C-1 $CaCl_2$+NH_3	3 days	55.7	1st day
		56	2nd day
		58	3rd day

Density, IC and Simple Weight Calculation for C-1 $CaCl_2+NH_3$

- Measured Density

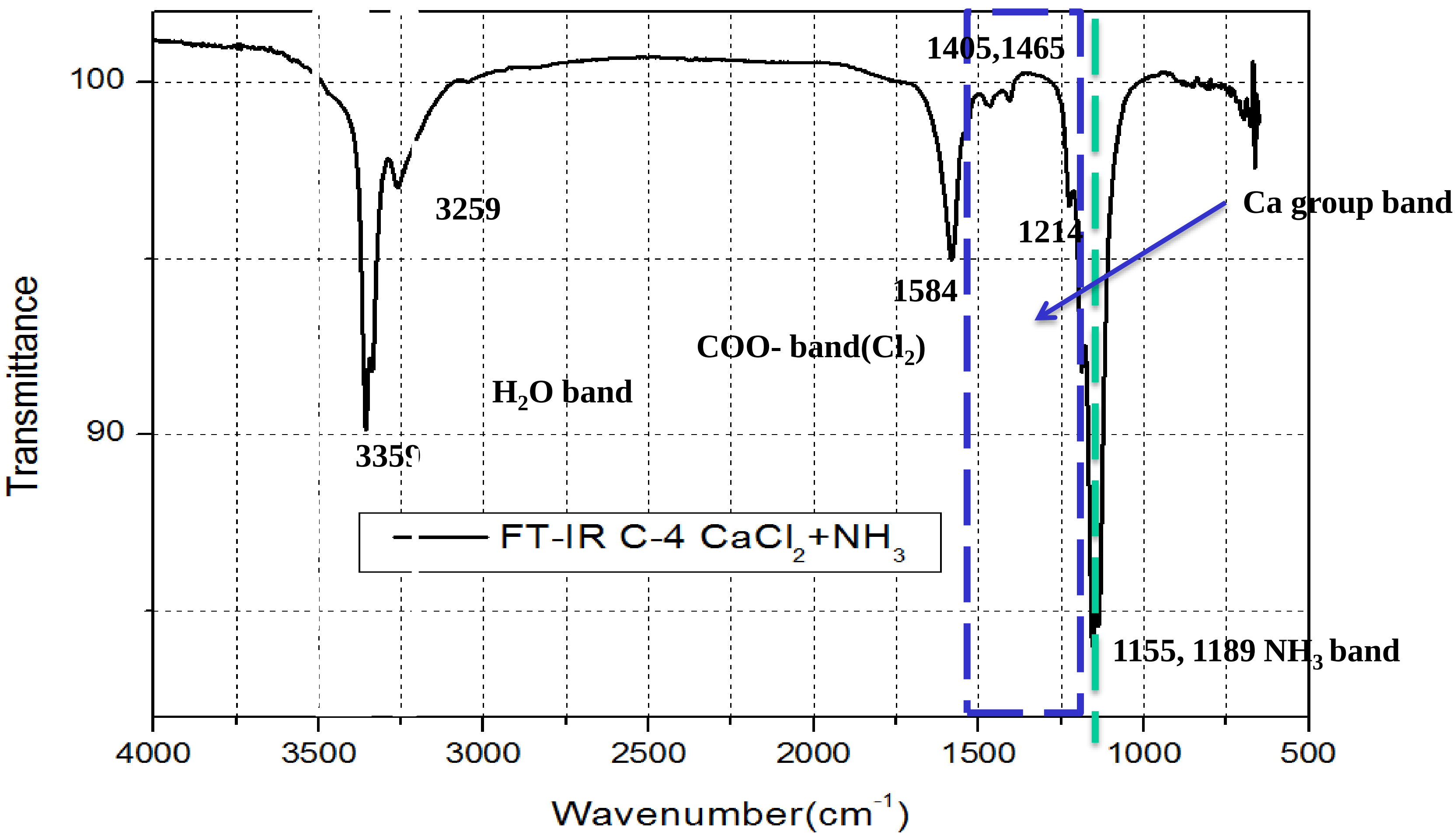
Materials for experiments	Run	Density (g/cm^3)	Average density (g/cm^3)	reference (g/cm^3)
C-1 $CaCl_2+NH_3$	1	1.22	1.22	1.19
	2	1.23		
	3	1.22		
	SD	0.00		
	CV	0.08		

IC	**Analytical Item**	**Unit**	**Contents**	**Result**
C-1 $CaCl_2+NH_3$	NH_3	%	-	31.3
			$Ca(NH_3)Cl_2$	184.11
			$Ca(NH_3)_2Cl_2$	92.05
			$Ca(NH_3)_8Cl_2$	56.84

- Comparison between IC result and simple weight calculation

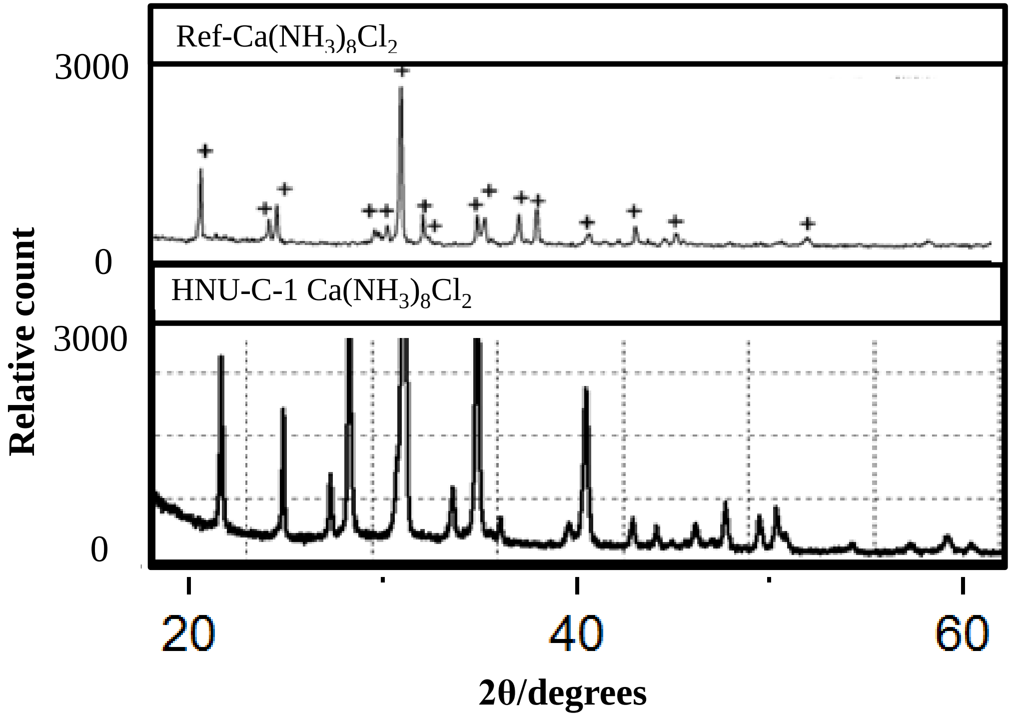
	IC(%)	Simple Weight Calculation(%)
C-1 $CaCl_2+NH_3$	56.84	58

FT-IR Spectra (C-1 $CaCl_2$ +NH_3)



- 1000 ~ 1200 cm^{-1} bands : NH_3 group of ammonia ion
- 1405 ~ 1465 cm^{-1} bands : Ca group
- 1584 cm^{-1} bands : COO- ion → Cl_2
- 3180 ~ 3360 cm^{-1} bands : H_2O

XRD Spectra (C-1 $CaCl_2$+ NH_3)



$$n\lambda = \frac{2d}{\sin\theta} - \frac{2d}{\tan\theta}\cos\theta = \frac{2d}{\sin\theta}(1-\cos^2\theta) = \frac{2d}{\sin\theta}\sin^2\theta$$

$$n\lambda = 2d \cdot \sin\theta$$

d : distance between atomic layers in a crystal

θ : certain angles of incidence

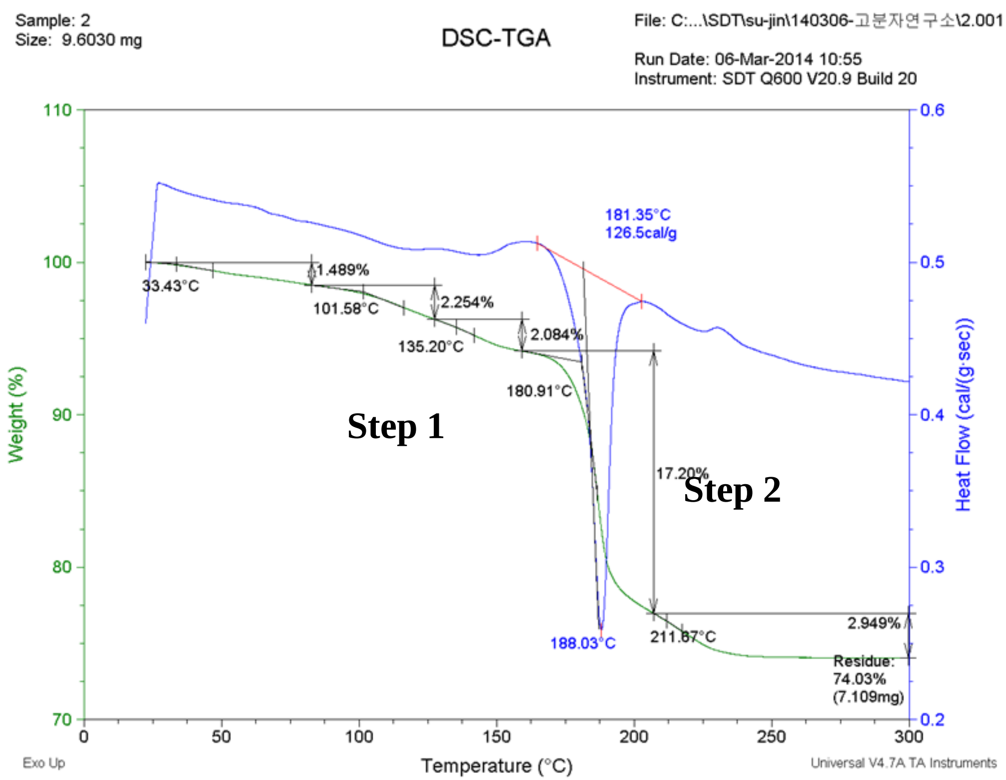
λ : wavelength of the incident X-ray beam

n : integer

2θ(deg)	**d spacing(Å)**
32.6	2.759
28.1	3.156
34.8	2.393

[Ref] R. Lin, Y. Liu, M. Gao, J. Wang, H. Ge and H. Pan, "Investigation on Performance of the Novel Ammonia-Based Hydrogen Storage Material $CaCl_2$," Journal of Inorganic Materials, Vol. 23, No. 5, pp. 1059-1063. 2008.

DSC-TGA Analysis (C-1 $CaCl_2$+ NH_3)



Sample	C-1 $CaCl_2$+NH_3
Temperature Range	15 ~ 300 ℃
Ramp Rate	1 ℃/min
Carrier Gas	N_2
Analysis Instrument	SDT Q600
Decomposition Temperature	33.43 ℃
Decomposition Temperature (reference)	32 ℃

$Ca(NH_3)_8Cl_2 \leftrightarrow Ca(NH_3)_2Cl_2+6NH_3$ (1)

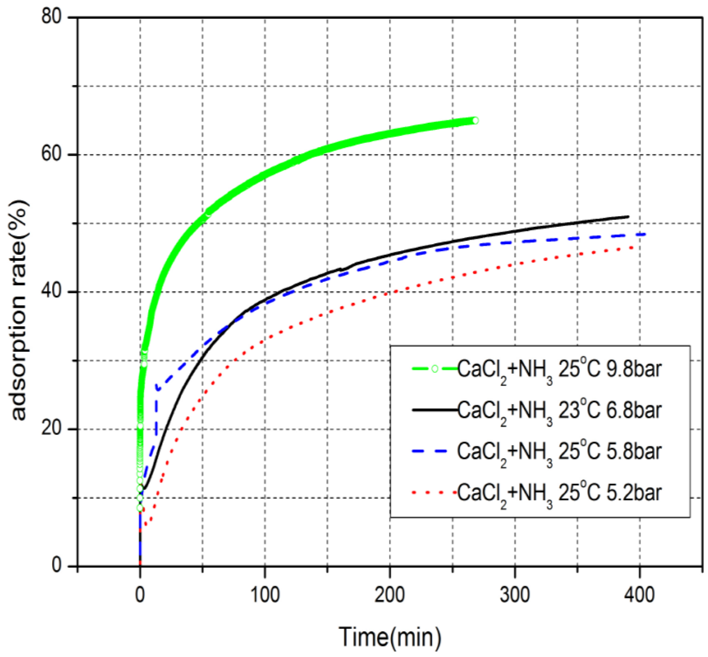
$Ca(NH_3)_2Cl_2 \leftrightarrow Ca(NH_3)Cl_2+NH_3$ (2)

$Ca(NH_3)Cl_2 \leftrightarrow CaCl_2+NH_3$ (3)

- Identify two step reactions.
- Because desorption starts initially around room temperature, it is very difficult to measure initial mass.
- 26% of initial sample weight is NH_3 gas, due to C-1 $CaCl_2$+NH_3 sample(58% of NH_3 adsorption rate).

Adsorption Rate of NH_3 from Charged $CaCl_2$ (Temperature & Pressure)

- Adsorption rate of NH_3 from charged $CaCl_2$ for different pressure with fixed temperature(about 23 ℃ and 25 ℃, 5.2 bar, 5.8 bar, 6.8 bar, and 9.8 bar)
- Anhydrous $CaCl_2$: 30 g
- At higher pressure with same temperature in adsorption region, adsorption rate of NH_3 is high.

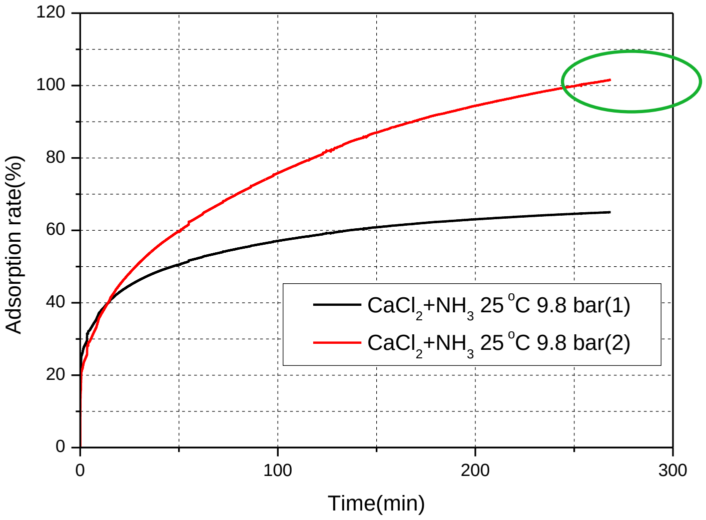


$$adsorption\ rate(\%) = \frac{m_{Ca(NH_3)_8Cl_2}}{M_{Ca(NH_3)_8Cl_2}}$$

New Test Procedure for Water Removal

- Same as previous test procedure.
- After insert $CaCl_2$ into the reactor in glove box, take a reactor out a glove box.
- Before supply ammonia gas, to remove remained water contents, heating a reactor for few hours, and exhaust a reactor of water.
- Cool down a reactor to room temperature, then supply ammonia gas
- Adsorption rate of NH_3 from charged $CaCl_2$ reached approximately 100%.

Adsorption rate of NH_3 from charged $CaCl_2$ for different test method



It might be residual gas beyond adsorption limit in reactor and tube.

By equation of state for an ideal gas, mass of residual gas(0.8 g) contributes to adsorption rate about 4%.

$$adsorption\ rate(\%) = \frac{m_{Ca(NH_3)_8Cl_2}}{M_{Ca(NH_3)_8Cl_2}}$$

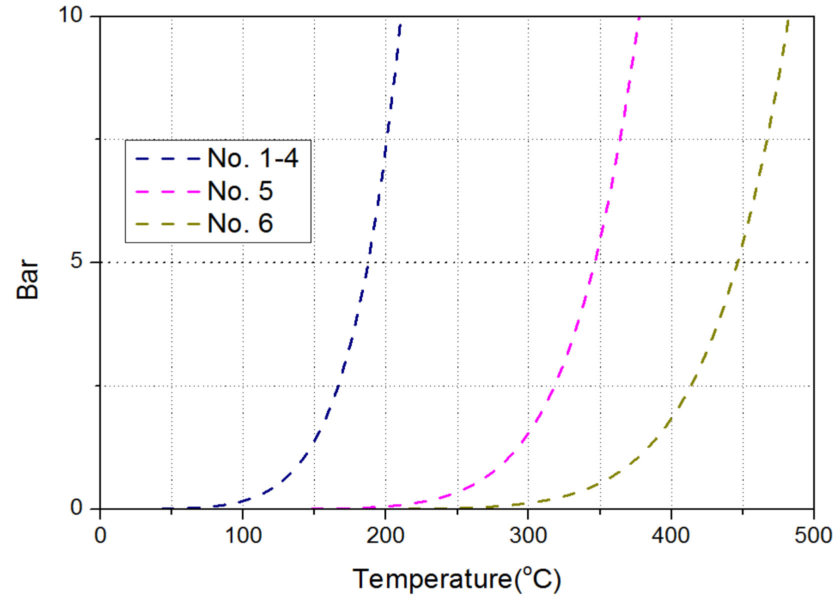
Magnesium Ammine Chloride

Desorption Chemistry

$Mg(NH_3)_6Cl_2 \leftrightarrow Mg(NH_3)_2Cl_2 + 4NH_3$ (1)

$Mg(NH_3)_2Cl_2 \leftrightarrow Mg(NH_3)Cl_2 + NH_3$ (2)

$Mg(NH_3)Cl_2 \leftrightarrow MgCl_2 + NH_3$ (3)



Equilibrium vapor pressure of NH_3 from charged $MgCl_2$.

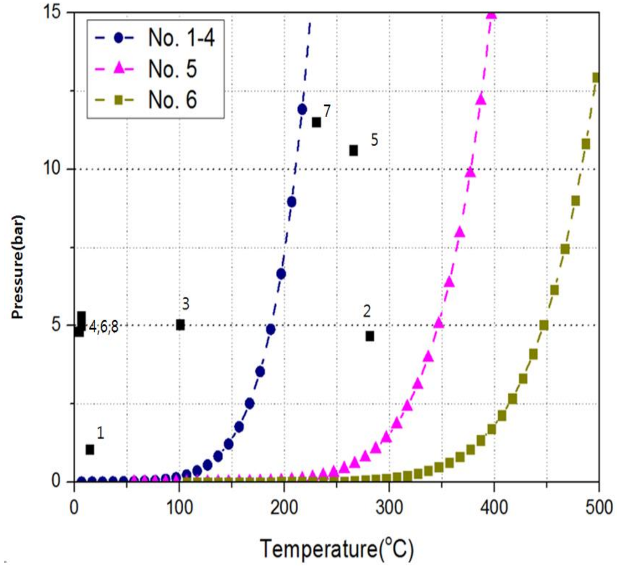
- Equilibrium Vapor Pressure Theory

$$\mathrm{Ln}\,P_{NH3} = \frac{-\Delta_{f,i}}{RT} + \frac{\Delta S_{f,i}}{R} \quad (1)$$

$$P_{NH3(T)} = \exp\left(\frac{-\Delta H_{f,i}}{RT} + \frac{\Delta S_{f,i}}{R}\right) \quad (2)$$

	NH_3 pressure at 25 °C	Desorption enthalpy	Desorption entropy
	bar	kJ/mol	kJ/(mol·K)
$Mg(NH_3)_6Cl_2$	0.0017		
No. 1-4		55.7	0.23
No. 5		74.9	0.23
No. 6		87	0.23

Test Conditions of $MgCl_2 + NH_3$



- Test protocol

M-1 : $MgCl_2 + (NH_3)$			
Condition	Temperature (°C)	Pressure(bar)	Time (h)
1	15	1.013	0
2	280	4.984	0.4
3	105	5.121	0.9
4	6	5.211	1st day –soaking
5	275	11.05	0.67
6	6.5	5.233	2nd day-soaking
7	220	12.5	0.67
8	6.6	5.3	3rd day-soaking-end

- Adsorption weight and adsorption rate calculation

M-1 $MgCl_2 + NH_3$			
		Weight(g)	Remarks
m0	Reactor	5956.56	
m1	Initial sample	45.49	
m2(=m0+m1)	Reactor + Initial sample	6002.05	
m3	Reactor + Initial sample + Adsorption capacity	6051.41	1st day
		6058.91	2nd day
		6061.61	3rd day
Δm(=m3-m2)	Adsorption capacity	49.36	1st day
		53.56	2nd day
		59.56	3rd day
Material	Test time	Adsorption rate(%)	Remarks
M-1 $MgCl_2+NH_3$	3 day	63	1st day
		65.9	2nd day
		67	3rd day

Density, IC and Simple Weight Calculation for M-1 $MgCl_2+NH_3$

- Measured Density

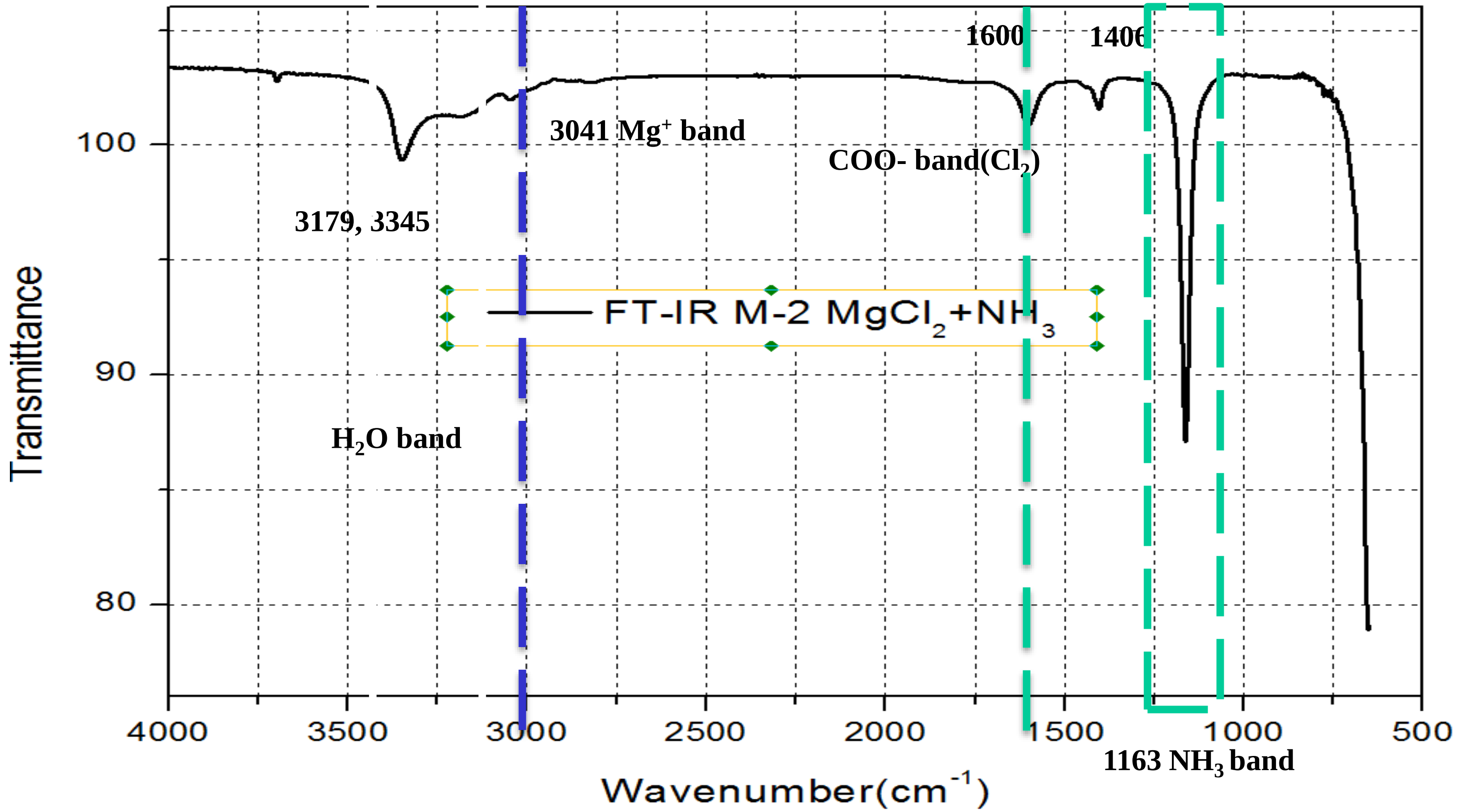
Materials for experiments	Run	Density (g/cm^3)	Average density (g/cm^3)	Average Volume(L)	reference (g/cm^3)
M-1 $MgCl_2$ + NH_3	1	1.58	1.58	0.0861	1.252
	2	1.58			
	3	1.58			
	SD	0.00			
	CV	0.15			

IC	Analytical Item	Unit	Contents	Result
M-1 $MgCl_2+NH_3$	NH_3	%	-	45.5
			$Mg(NH_3)Cl_2$	267.64
			$Mg(NH_3)_2Cl_2$	133.82
			$Mg(NH_3)_6Cl_2$	77.23

- Comparison between IC result and simple weight calculation

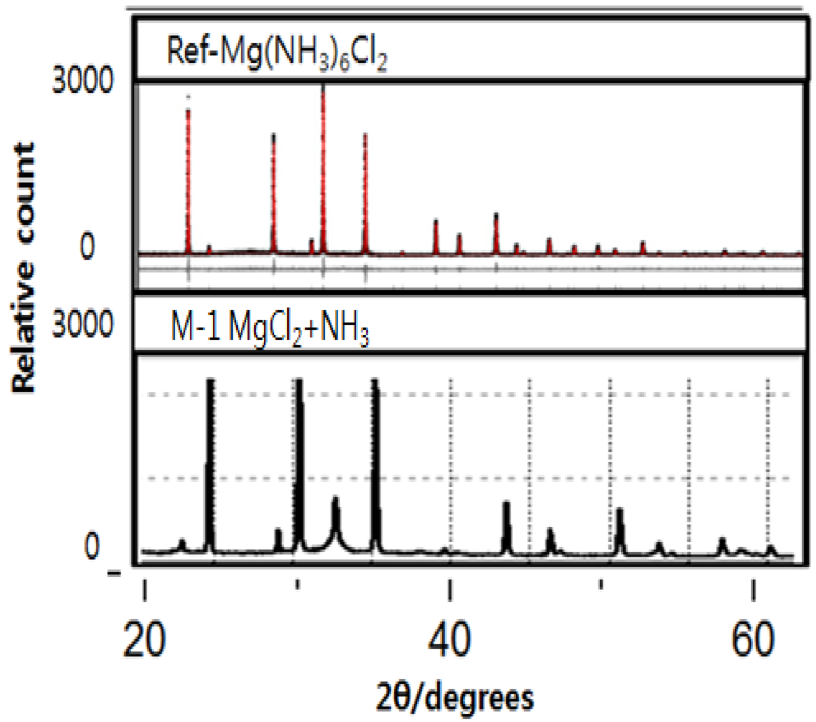
	IC(%)	Simple Weight Calculation(%)
M-1 $Mg(NH_3)_6Cl_2$	77.23	67

FT-IR Spectra (M-1 $MgCl_2$ +NH_3)



- 1000 ~ 1200 cm^{-1} bands : NH_3 group of ammonia ion
- 1584 cm^{-1} bands : COO- ion → Cl_2
- 3041 cm^{-1} bands : Mg+
- 3180 ~ 3360 cm^{-1} bands : H_2O

XRD Spectra (M-1 $MgCl_2$+ NH_3)



$$n\lambda = \frac{2d}{\sin\theta} - \frac{2d}{\tan\theta}\cos\theta = \frac{2d}{\sin\theta}(1-\cos^2\theta) = \frac{2d}{\sin\theta}\sin^2\theta$$

$$n\lambda = 2d \cdot \sin\theta$$

d : distance between atomic layers in a crystal

θ : certain angles of incidence

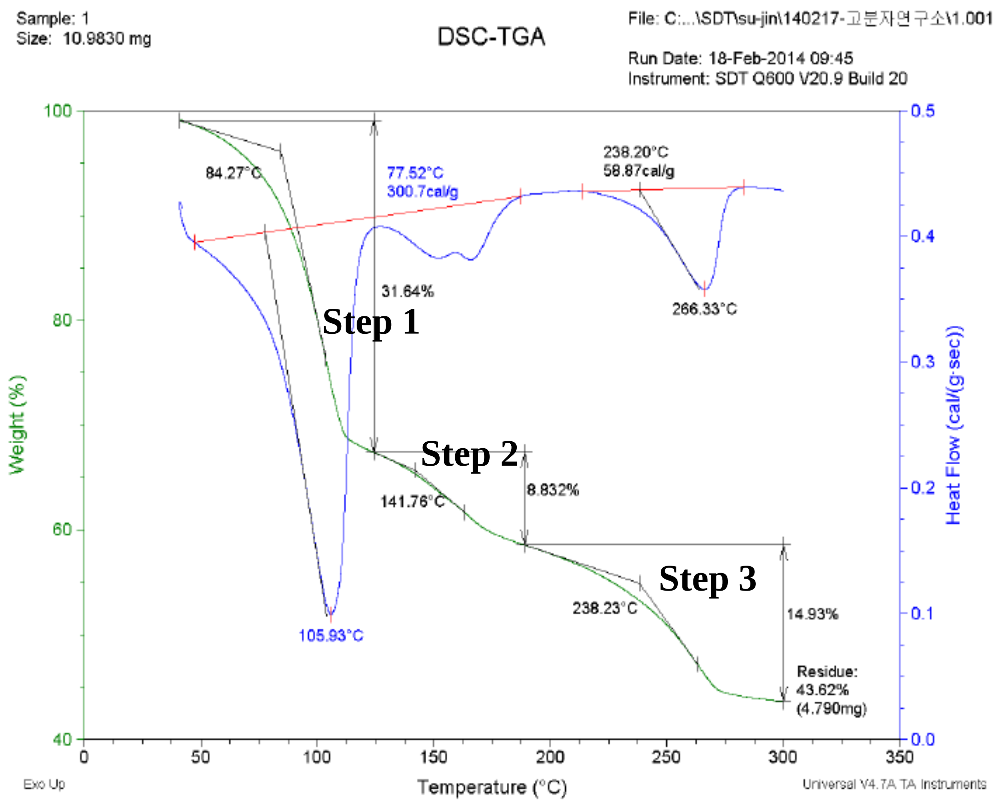
λ : wavelength of the incident X-ray beam

n : integer

2θ(deg)	**d spacing(Å)**
35.12	5.699
30.4	2.938
24.74	3.552

[Ref] M. Owen, M, Royse, P. Edwards, I.F. David, “The Structure and Desorption Properties of the Ammines of the Group II Halides,” ELSEVIER, *Chemical Physics*, Vol. 427, pp. 38~43, 2013.

DSC-TGA Analysis (M-1 $MgCl_2$+ NH_3)



Sample	M-1 $MgCl_2$+NH_3
Temperature Range	15 ~ 300 ℃
Ramp Rate	1 ℃/min
Carrier Gas	N_2
Analysis Instrument	SDT Q600
Decomposition Temperature	84.27 ℃
Decomposition Temperature (Reference)	142 ℃

$Mg(NH_3)_6Cl_2 \leftrightarrow Mg(NH_3)_2Cl_2+4NH_3$ (1)

$Mg(NH_3)_2Cl_2 \leftrightarrow Mg(NH_3)Cl_2+NH_3$ (2)

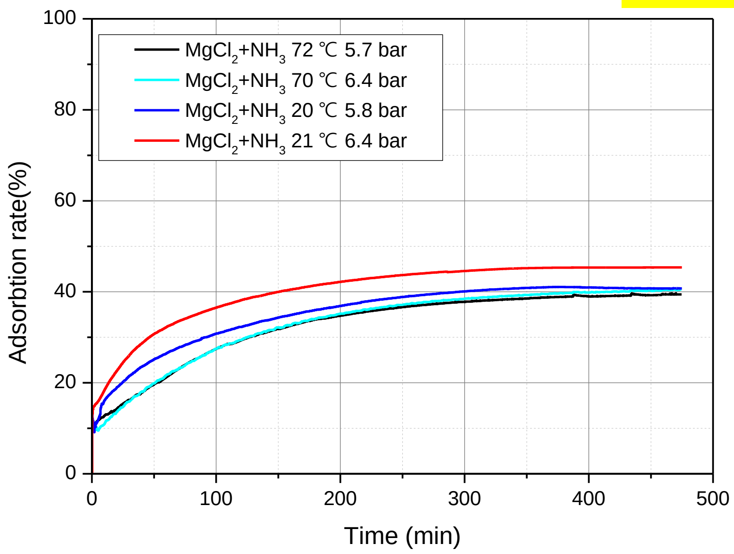
$Mg(NH_3)Cl_2 \leftrightarrow MgCl_2+NH_3$ (3)

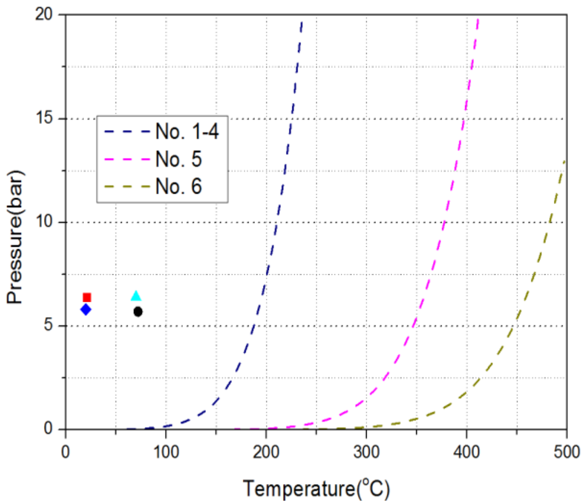
- Identify three step reaction.
- 56.38% of initial sample weight is NH_3 gas, due to M-1 $MgCl_2$+NH_3 sample(67% of NH_3 adsorption rate).

Adsorption Rate of NH_3 from Charged $MgCl_2$ (Temperature & Pressure)

- Adsorption rate of NH_3 from charged $MgCl_2$ for different pressure with fixed temperature(about 20 ℃ and 70 ℃, 5.8 bar, and 6.4 bar)
- Anhydrous $MgCl_2$: 30 g
- At lower temperature and higher pressure in adsorption region, adsorption rate of NH_3 is high.

$$adsorption\ rate(\%) = \frac{m_{Mg(NH_3)_6Cl_2}}{M_{Mg(NH_3)_6Cl_2}}$$



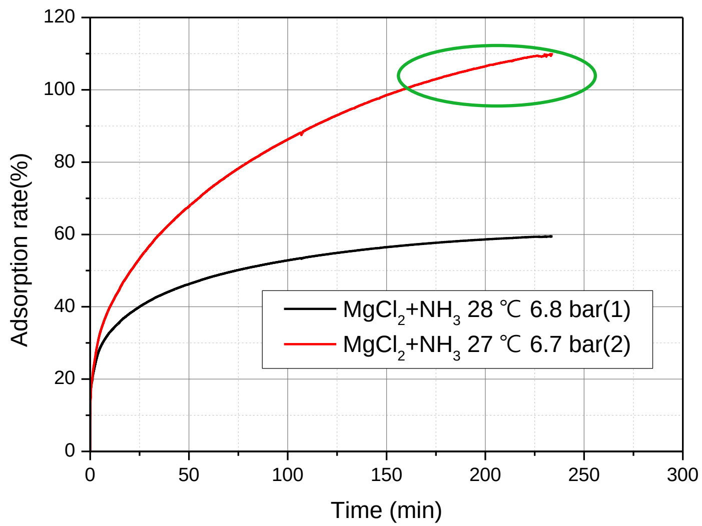


Equilibrium vapor pressure curve of NH_3

New Test Procedure for Water Removal

- Same as previous test procedure.
- After insert $MgCl_2$ into the reactor in glove box, take a reactor out a glove box.
- Before supply ammonia gas, to remove remained water contents, heating a reactor for few hours, and exhaust a reactor of water.
- Cool down a reactor to room temperature, then supply ammonia gas
- Adsorption rate of NH_3 from charged $MgCl_2$ reached approximately 100%.

Adsorption rate of NH_3 from charged $MgCl_2$ for different test method



It might be residual gas beyond adsorption limit in reactor and tube.

By equation of state for an ideal gas, mass of residual gas(5.25 g) contributes to adsorption rate about 12.1%.

$$adsorption\ rate(\%) = \frac{m_{Mg(NH_3)_6Cl_2}}{M_{Mg(NH_3)_6Cl_2}}$$

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Concluding Remarks (1/2)

To make calcium ammine chloride and magnesium ammine chloride in lab-scale, simple reactor and glove box was designed and built with ammonia gas tank, nitrogen gas tank, regulator, and DAQ with temperature and pressure sensors.

- Basic test conditions of charging ammonia gas to anhydrous calcium chloride and anhydrous magnesium chloride are chosen from equilibrium vapor pressure by Van't Hoff plot based on thermodynamic properties of materials.
- Synthetic method of calcium ammine chloride and magnesium ammine chloride were studied for different durations, temperatures, and pressures with proper ammonia gas charged, as a respect of ammonia gas adsorption rate(%) for simple weight calculations which were confirmed by IC.
- Lab-made calcium ammine chloride and magnesium ammine chloride were analyzed by TGA and DSC to clarify decomposition step in the equations of chemical reaction.

Concluding Remarks (2/2)

- To understand material characteristics for lab-made calcium ammine chloride and magnesium ammine chloride, DA, XRD and FT-IR analysis were performed using the published data available in literature.

- From analytical results, the water content in the lab-made calcium ammine chloride and magnesium ammine chloride can be recognized.

- Maxium pressures of test conditions are restricted to ambient temperature, because ammonia gas is supplied by liquid ammonia in a tank.

- At lower temperature and higher pressure in adsorption region, adsorption rate of NH_3 is high.

- A new test procedure for water removal was proposed, by which the adsorption rate of lab-made sample was found to be approximately 100%.

Acknowledgments

- This research was supported by the Center for Environmentally Friendly Vehicle (CFEV) as a Global-Top Project of the Ministry of Environment, Korea (KMOE)

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Thank you for your attention !

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