Absorption and Desorption Characteristics of NH_3 with Metal Chlorides for Ammonia Storage

Introduction

Ammonia (NH_3) ▪▪ **Various applications** — Raw material of chemical substances; Fertilizer for agriculture; Refrigerant for air conditioning

In the future **Energy carrier for hydrogen utilization system**

◎ High hydrogen content of 17.8 wt%

◎ Easy to store, transport and handle it by liquification

Ammonia storage by liquification is very convenient,

But…

▲ High pressure (0.86 MPa at 293 K)

▲ Risk of leakage during storage and in case of emergency

▲ High toxicity and danger if leakage occurs

To solve this problem

Ammonia storage by **Absorption/Desorption Reactions of NH_3 with $MeCl_2$**

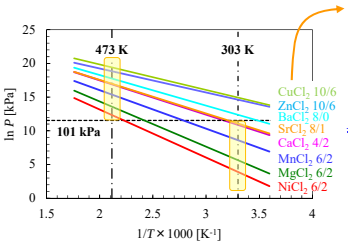
$$MeCl_2 \cdot mNH_3 + nNH_3 \Leftrightarrow MeCl_2 \cdot (m+n)NH_3$$

◎ High stability by storing NH_3 in the form of chemical substances

◎ Handling under atmospheric or reduced pressures

◎ High NH_3 storage

◎ Utilization of low-temperature heat as regeneration heat source



From **thermodynamics**,

Mn, Ni, Mg, Sr and Ca chlorides might be suitable for NH_3 storage.

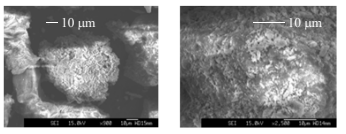
In this study

Thermogravimetric studies were performed under various reaction temperatures and NH_3 partial pressures for these candidate reactions.

Experimental

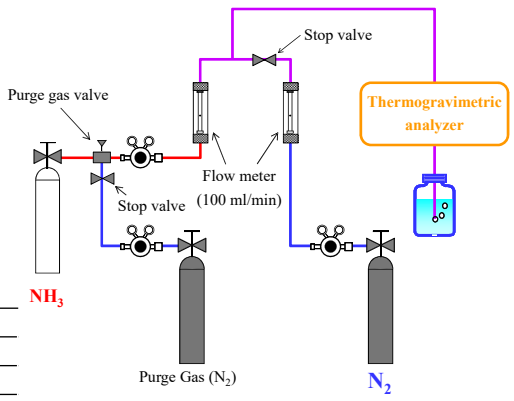
Starting material:

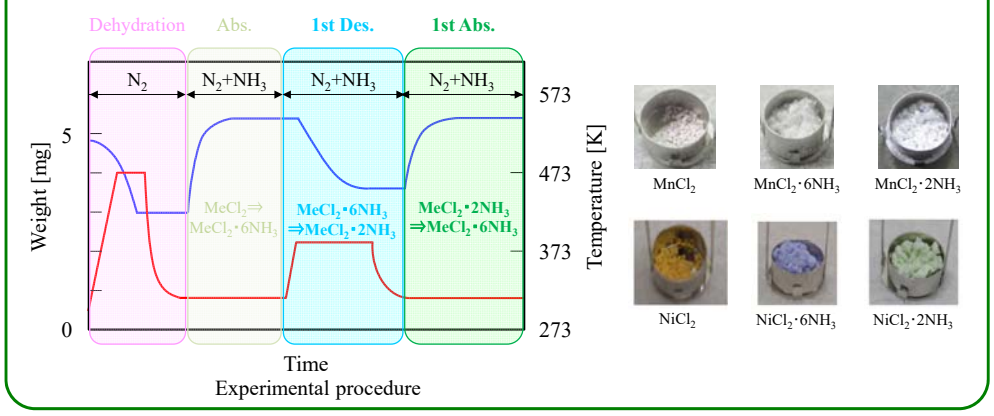
$MnCl_2 \cdot 4H_2O$	(Purity:>99.9 %)
$NiCl_2$	(Purity:>95.0 %)
$SrCl_2 \cdot 6H_2O$	(Purity:>99.9 %)
LiCl	(Purity:>98.0 %)



$MnCl_2$ $NiCl_2$

		$MnCl_2$	$NiCl_2$
Temperature, T [K]	Abs.	303-333	303-383
	Des.	343-363	383-443
NH_3 partial pressure, P [kPa]	Abs.	0.84-84	
	Des.	0.84-42	
Initial particle size, d_p [mm]		63-75	300-355

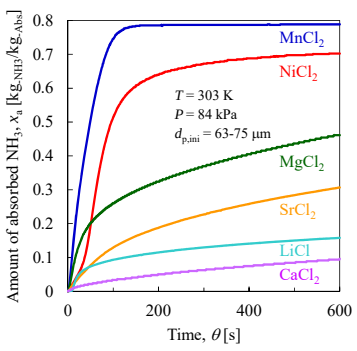




Results & Discussion

Reaction Characteristics of NH_3 with Metal Chlorides

～ Selection of candidate reaction for NH_3 storage ～



$MnCl_2$

Fastest absorption rate

Highest NH_3 absorptivity : 0.79 $kg_{\text{-}NH3}/kg_{\text{-}MnCl2}$ (5.8 $mol_{\text{-}NH3}/mol_{\text{-}MnCl2}$)

$NiCl_2$

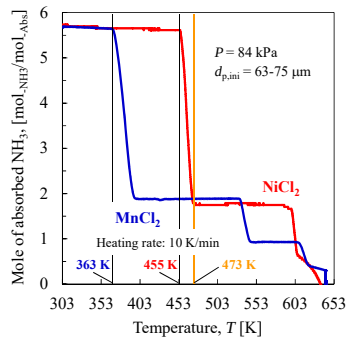
Faster absorption rate

Higher NH_3 absorptivity : 0.70 $kg_{\text{-}NH3}/kg_{\text{-}MnCl2}$ (5.36 $mol_{\text{-}NH3}/mol_{\text{-}NiCl2}$)

NH_3 storage density : **0.81 $g_{\text{-}NH3}/cm^3_{\text{-}NiCl2\ packed\ bed}$** ($\rho_{NiCl2 \cdot 6NH3}$=2.08 g/cm³, Porosity, ε=0.26) (cf:NH_3 liquid density : **0.64 g/cm³**)

$MnCl_2$ & $NiCl_2$ are promising reaction for ammonia storage.

～ Determination of reaction system of Mn, $NiCl_2$/NH_3 ～



$MnCl_2$/NH_3

$MnCl_2 \cdot 6NH_3 \Rightarrow MnCl_2 \cdot 2NH_3$: 363-393 K

$MnCl_2 \cdot 2NH_3 \Rightarrow MnCl_2$: > 530 K

$NiCl_2$ /NH_3

$NiCl_2 \cdot 6NH_3 \Rightarrow NiCl_2 \cdot 2NH_3$: 455-473 K

$NiCl_2 \cdot 2NH_3 \Rightarrow NiCl_2$: >635 K

To utilize low-temp. heat < 473 K for regeneration

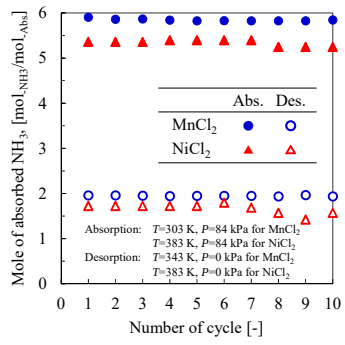
$MnCl_2 \cdot 2NH_3 \Leftrightarrow MnCl_2 \cdot 6NH_3$

$NiCl_2 \cdot NH_3 \Leftrightarrow NiCl_2 \cdot 6NH_3$

are suitable for NH_3 storage.

Especially, $MnCl_2$/NH_3 can regenerate **below 393 K**.

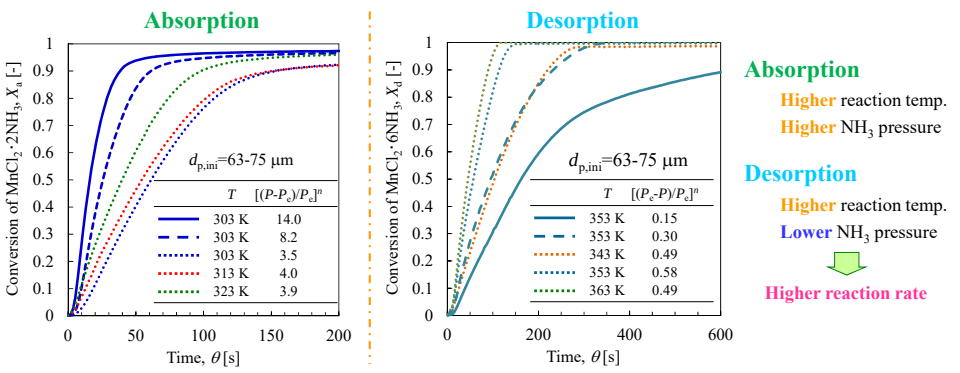
～ Repeatability of $MeCl_2 \cdot 2NH_3/6NH_3$ reaction ～



Both $MnCl_2$ and $NiCl_2$ seems to have repeatability of abs./des. reactions.

Kinetic Study of Reactions between Mn, $NiCl_2$ and NH_3

～ Effect of temperatures & NH_3 pressures on reaction rate of $MnCl_2$/NH_3 System ～



Absorption

Higher reaction temp.

Higher NH_3 pressure

Desorption

Higher reaction temp.

Lower NH_3 pressure

Higher reaction rate

Reaction rate expression

Assumption : Chemical-reaction is rate-determining step.

Grain model with the assumption of the presence of a reaction intermediate is applicable.

Reaction rate expression :

$$\frac{dX}{d\theta} = k(1-X)^{2/3}\left(\frac{\Delta P}{P_e}\right)^n$$

$\Delta P = P - P_e$ for **Absorption**

$\Delta P = P_e - P$ for **Desorption**

$$1-(1-X)^{1/3} = \frac{1}{3}k\left(\frac{\Delta P}{P_e}\right)^n t$$

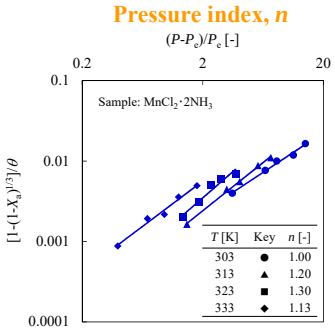
$MnCl_2 \cdot 2NH_3/6NH_3$

$$\ln P_e\,[Pa] = -\frac{47416}{R}\frac{1}{T} + \frac{228.07}{R}$$

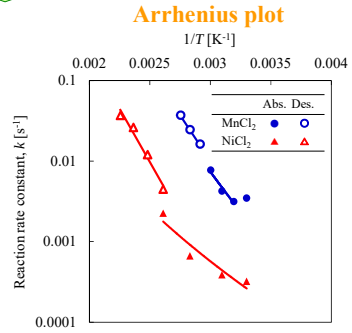
$NiCl_2 \cdot 2NH_3/6NH_3$

$$\ln P_e\,[Pa] = -\frac{59217}{R}\frac{1}{T} + \frac{227.75}{R}$$

Pressure index, n



Arrhenius plot



	$MnCl_2$	$NiCl_2$
Absorption	$k_a = 8.71\times10^3 \exp\left(-\frac{38.7\times10^3}{RT}\right)$, n=1.16	$k_a = 2.19\times10^0 \exp\left(-\frac{22.8\times10^3}{RT}\right)$, n=0.95
Desorption	$k_d = 5.11\times10^4 \exp\left(-\frac{42.7\times10^3}{RT}\right)$, n=4.48	$k_d = 3.80\times10^4 \exp\left(-\frac{50.5\times10^3}{RT}\right)$, n=3.60

Conclusion

- Manganese chloride and nickel chloride were promising materials in terms of rapid NH_3 storage and high storage density.
- Reversible reaction between $MeCl_2 \cdot 2NH_3$ and $MeCl_2 \cdot 6NH_3$ (Me=Mn and Ni) is effective to release NH_3 using low-temperature thermal energy below 473 K. Especially, $MnCl_2 \cdot 2/6NH_3$ system can regenerate below 393 K.
- $MeCl_2 \cdot 2NH_3/MeCl_2 \cdot 6NH_3$ (Me=Mn and Ni) reversible reactions were maintained the durability at least within 10 cycles.
- A reaction rate expressions on the basis of grain model were determined for NH_3 absorption of $MeCl_2 \cdot 2NH_3$ and desorption of NH_3 form $MeCl_2 \cdot 6NH_3$ (Me=Mn and Ni) , respectively.

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