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Thermodynamic properties of metal amides determined by ammonia pressure-composition isotherms

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ABSTRACT

Thermodynamic properties of $Mg(NH_2)_2$ and $LiNH_2$ were investigated by measurements of NH_3 pressure-composition isotherms (PCI). Van't Hoff plot of plateau pressures of PCI for decomposition of $Mg(NH_2)_2$ indicated the standard enthalpy and entropy change of the reactions were $\Delta H^\circ = (120 \pm 11)\ \mathrm{kJ \cdot mol^{-1}}$ (per unit amount of NH_3) and $\Delta S^\circ = (182 \pm 19)\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ for the reaction: $Mg(NH_2)_2 \rightarrow MgNH + NH_3$, and $\Delta H^\circ = 112\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta S^\circ = 157\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ for the reaction: $MgNH \rightarrow (1/3)Mg_3N_2 + (1/3)NH_3$. PCI measurements for formation of $LiNH_2$ were carried out, and temperature dependence of plateau pressures indicated $\Delta H^\circ = (-108 \pm 15)\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta S^\circ = (-143 \pm 25)\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ for the reaction: $Li_2NH + NH_3 \rightarrow 2LiNH_2$.

1. Introduction

Thermodynamic properties of metal amides were estimated from ammonia NH_3 pressure-composition (p-C) isotherms (PCI) for decomposition and formation of metal amides. Metal amides react with metal hydrides to desorb hydrogen and these reactions have been paid attention as new hydrogen storage systems since Chen *et al.'s* report [1]. Hydrogen desorbed from these compounds contaminated by a small amount of NH_3 originated from decomposition of the amides themselves, which would be a problem for an application of these systems [2,3]. Therefore, thermodynamic properties of the metal amides are important, and the thermodynamics of (metal + N + H) system should be discussed by taking account of the thermodynamics of elementary reactions.

The chemistry of the alkali and alkaline earth metal amides has been the subject of a large number of investigations [4,5]. Thermal decomposition properties of metal amides under inert gas flow (or in vacuum) have been investigated. Magnesium amide $Mg(NH_2)_2$ decomposes to magnesium imide MgNH and NH_3 by heating to $T = (573\text{ to }673)$ K through the following reaction [6]:

$$Mg(NH_2)_2 \rightarrow MgNH + NH_3 \tag{1}$$

Then, magnesium imide decomposes into magnesium nitride Mg_3N_2 with NH_3 release at more than $T = 623$ K as follows:

$$MgNH \rightarrow (1/3)Mg_3N_2 + (1/3)NH_3 \tag{2}$$

Lithium amide $LiNH_2$ decomposes to lithium imide Li_2NH and NH_3 at temperatures of (573 to 673) K [7,8]:

$$2LiNH_2 \rightarrow Li_2NH + NH_3 \tag{3}$$

and imide decomposes into lithium nitride at higher temperatures. In addition, the enthalpies of formation of $LiNH_2$ and Li_2NH have been reported from the measurements of the heat of dissolution [9].

Thermodynamic properties (e.g. standard enthalpy or entropy change of reaction, ΔH° and ΔS°) of (metal + hydrogen) systems have been investigated by measuring p-C isotherms [10]. The p-C isotherms of decomposition (and formation) of $LiNH_2$ to (from) Li_2NH at $T = 573$ K and $T = 673$ K have been reported in 1951 [8]. Liu *et al.* [11] has reported the results of p-C isotherms of decompositions of $LiNH_2$ and $Mg(NH_2)_2$. These measurements were performed above the melting point of $LiNH_2$ ($T = 653$ K) and $Mg(NH_2)_2$ ($T = 633$ K). $LiNH_2$ volatilizes around $T = 673$ K and may be sublimed under pressure in an ammonia atmosphere [12], which may prevent accurate determination of equilibrium pressures. In the present work, all p-C isotherms were carried out below the melting point of the metal amides. Temperature dependences of plateau pressures p were measured to determine ΔH° and ΔS° of the reactions for the decomposition or formation of the metal amides from van't Hoff equation ($\ln (p/p^\circ) = -\Delta H^\circ/$

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$RT + \Delta S^\circ/R$, where p° is standard pressure 0.1 MPa, R the gas constant and T absolute temperature).

Decomposition reaction of ammonia to nitrogen and hydrogen ($2NH_3 \rightarrow N_2 + 3H_2$) should be considered during the NH_3 PCI measurements. In the viewpoint of thermodynamics, equilibrium NH_3 conversion to N_2 and H_2 is >90% above $T = 573$ K under normal pressure [13]. Therefore, amounts of generated H_2 were measured by gas chromatography (GC), and net NH_3 pressures were evaluated.

2. Experimental

$Mg(NH_2)_2$ was synthesized by reacting MgH_2 under gaseous NH_3 flow ($p = 0.5$ MPa, at a flow rate of $25\ ml \cdot min^{-1}$) at $T = 473$ K for 14 days ($MgH_2 + 2NH_3 \rightarrow Mg(NH_2)_2 + 2H_2$). $LiNH_2$ (Sigma–Aldrich Co., 95%) was heated up to $T = 723$ K under vacuum for 10 h to derive Li_2NH. Li_2NH was activated by ball-milling (Fritsch, P7) under Ar atmosphere for 2 h and was provided for PCI measurement of formation of $LiNH_2$. All handling of chemicals took place in a glove box filled with purified Ar.

NH_3 *p-C* isotherms were measured using a Sieverts type apparatus. Prior to the sample measurement, blank *p-C* isotherms were measured, and as a result, the total pressure was found to increase slightly due to the NH_3 decomposition.

Desorption PCI: ~100 mg sample was loaded in a sample holder (10 ml volume). The system was evacuated, and sufficient amount of NH_3 (5 N) gas was introduced into the system. The sample cell was heated up to a measurement temperature with a heating rate of $5\ K \cdot min^{-1}$ and the temperature was held constant. Pressure change was monitored by a pressure transducer (GE Druck, PDCR-4000) and data acquisition system. After stabilizing the pressure (waiting time: 1 to 12 h), gas in the reservoir (61 or 14 ml volume) was introduced to a gas chromatograph (GC-14B, Shimadzu Corp.) to determine H_2 and N_2 amounts from GC peak intensities. Pure H_2 (7 N) and N_2 (99.99995%) gases are used for calibration of the GC peak area and gas pressure. Net NH_3 equilibrium pressure and the amount of decomposed ammonia were estimated by subtracting H_2 and N_2 pressures from total pressure, as a result, one data point of PCI curve was derived. Stepwise decrease in NH_3 pressure followed by waiting for equilibrium and GC measurement were continued. In the case of waiting time exceeded 12 h, measurement went next step, because such slow pressure increase may be caused by NH_3 decomposition.

Absorption PCI: ~50 mg sample was loaded in the sample holder and the system was evacuated and then heated. The NH_3 gas was introduced to apply stepwise increase in the pressure. At each pressure, waiting time of 15 min was adopted to realize the equilibrium state, because the absorption reaction showed fast kinetics. It was difficult to perform the GC measurement for the analysis of the gas composition, since equilibrium pressures were very low.

Powder X-ray diffraction (RINT-2500V, Rigaku, Cu Kα radiation) measurement was carried out at room temperature to identify phases before and after the PCI measurements.

3. Results and discussion

The *p-C* isotherms of the decomposition of $Mg(NH_2)_2$ to MgNH were measured at lower temperatures than the melting point of $Mg(NH_2)_2$, i.e. $T = 633$ K. Total pressure gradually increased during the desorption measurement with a rate of 0.2 to $1\ kPa \cdot h^{-1}$, which may be caused by decomposition of NH_3 itself. Therefore, the GC measurement was carried out to subtract H_2 and N_2 contribution to the total pressure and actual NH_3 pressure was estimated. Figure 1 shows NH_3 *p-C* isotherms of decomposition of $Mg(NH_2)_2$ at $T = (583, 603, \text{and } 623)$ K. Plateau regions which corresponded to the decomposition of amide phase to imide phase appeared, and the plateau pressures, i.e., the values of the pressures at the mid-point of the plateau, are $p = (6.0, 15.6, \text{and } 29.4)$ kPa at $T = (583, 603, \text{and } 623)$ K, respectively. Plateau region of the decomposition of MgNH to Mg_3N_2 was not observed, therefore, the plateau pressure of the decomposition of imide to nitride phase may be too low at these temperatures. For the isotherms at temperatures of (623 and 583) K, the lengths of the plateau regions did not reach a theoretical value (25%). It could be caused by decrease in surface or bulk activity of a part of the powder sample by long time sintering. We suppose a small amount of deactivated powders have no significant effect for the plateau pressure. XRD profiles of the sample after desorption PCI measurement at $T = 603$ K are shown in figure 2a, which shows the presence of MgNH phase after the PCI measurement.

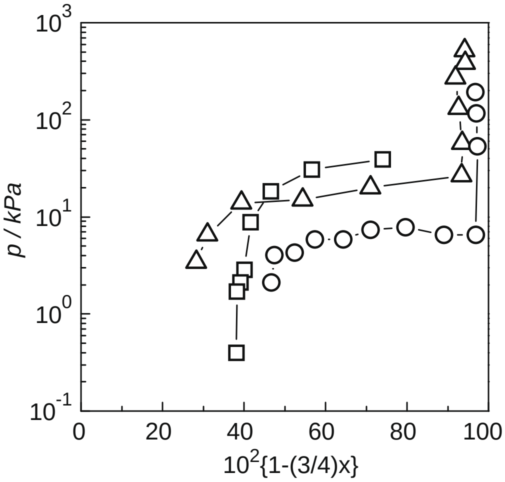

FIGURE 1. Pressure-composition isotherms for decomposition of $Mg(NH_2)_2$ at $T = 583$ K (○), $T = 603$ K (△), and $T = 623$ K (□). The horizontal axis shows the percent of ammonia left to desorb, where xNH_3 desorbs through the following reaction: $Mg(NH_2)_2$ (100%) → MgNH (25%) + NH_3 → (1/3)Mg_3N_2 (0%) + (4/3)NH_3.

Higher temperature was applied to measure *p-C* isotherms of decomposition of MgNH to Mg_3N_2. Figure 3 shows the PCI curves of the reaction (2) at $T = (663, 683, \text{and } 693)$ K. The plateau regions which corresponded to the decomposition of imide phase to nitride phase appeared for the measurements at temperatures of (663 and 683) K, and the values of the plateau pressures are $p = 8.0$ kPa at $T = 663$ K, $p = 14.9$ kPa at $T = 683$ K. After the desorption PCI measurement at $T = 693$ K, main phase was Mg_3N_2 in XRD profile as shown in figure 2b.

The NH_3 desorption plateau pressures in van't Hoff plot ($\ln(p/p^\circ)$ *vs.* T^{-1}) are shown in figure 4a and b. The slope of $\ln(p/p^\circ)$ and the intercept corresponds to ΔH° and ΔS°, respectively. The results are $\Delta H^\circ = (120 \pm 11)\ kJ \cdot mol^{-1}$ and $\Delta S^\circ = (182 \pm 19)\ J \cdot mol^{-1} \cdot K^{-1}$ for the reaction (1), and $\Delta H^\circ = 112\ kJ \cdot mol^{-1}$ and $\Delta S^\circ = 157\ J \cdot mol^{-1} \cdot K^{-1}$ for the reaction (2). Here, we define the unit as per mole amount of NH_3 for the reactions. Liu *et al.* [11] have reported much higher NH_3 equilibrium pressure ($p =$ ca. 200 kPa at $T = 623$ K) for the decomposition of $Mg(NH_2)_2$ to MgNH in the temperature range of $T = (613 \text{ to } 643)$ K, and calculated smaller enthalpy change of NH_3 generation ($\Delta H^\circ_{ref} = 40.8\ kJ \cdot mol^{-1}$). Such high pressures could come from the decomposition of NH_3 to H_2 and N_2, and van't Hoff plot of the total pressures could not show ΔH° of the decomposition of the amide. In our work, the partial pressures of H_2 and N_2 were calculated by the GC measurement.

Using ΔH° and ΔS° values above and literature values of the standard enthalpy $\Delta^f H^\circ$ of formation and standard entropy S° for