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Relation	



Pseudo Catalytic Ammonia Synthesis by Lithium-Tin Alloy

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Abstract

In this work, nitrogenation, ammonia generation, regeneration reactions of lithium-tin alloy is investigated as pseudo catalytic process of ammonia synthesis. $\text{Li}_{17}\text{Sn}_4$ synthesized by thermochemical method at 500 °C can react with 0.1 MPa of N_2 below 400 °C. Nano or amorphous lithium nitride would be formed by the nitrogenation. By reaction of the nitrogenated samples and H_2 , ammonia is generated at 300 °C under 0.1 MPa. The initial alloy phase $\text{Li}_{17}\text{Sn}_4$ is regenerated below 350 °C from the products after the ammonia generation process. Based on the above three step process, ammonia can be pseudo-catalytically synthesized from N_2 and H_2 below 400 °C under ambient pressure. Furthermore, the reactivity for the ammonia synthesis using Li-Sn alloy is preserved during the NH_3 synthesis cycles due to the characteristic reaction process based on the Li extraction and insertion.

Keywords: Ammonia, Lithium alloy, Catalytic Process, Nitrogen, Hydrogen

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Introduction

So far, ammonia (NH_3) is mainly synthesized as a material of chemical fertilizer by Haber–Bosch process, which is well known as a mass production technique of NH_3 . To effectively produce massive NH_3 , high temperature and pressure process is used from thermodynamic and kinetic reasons. In addition, catalysts are required to dissociate nitrogen (N_2) and hydrogen (H_2) molecules, and currently the iron based catalyst is utilized because of low cost and suitable activity. On the other hand, research on the catalysts for the NH_3 synthesis process are continued¹⁻⁵. In recent years, NH_3 is recognized as an attractive energy storage and transportation medium for effective utilization of fluctuated natural energy because of the high gravimetric and volumetric energy density⁶. In this situation, the small-scale and distribution-type systems of NH_3 synthesis are required because of unsuitability for downsizing the Haber–Bosch process. Therefore, the NH_3 synthesis process should be operated at lower temperature and pressure than those of conventional ones.

With increase in the above interests for NH_3 recently, various types of catalysts are proposed to synthesize NH_3 with highly activity or under mild conditions, Ruthenium (Ru)-based catalysts^{7, 8}, Ru loaded electrides⁹⁻¹¹, Ru-Cs catalyst with electric field¹², complexes¹³⁻¹⁸, oxihydride¹⁹, molten-sodium²⁰, transition-metal composite²¹, other compounds such as carbide and nitride²²⁻²⁸, and systems including electrochemical process^{29, 30}.

In addition, the NH_3 synthesis processes based on chemical reaction using lithium nitride (Li_3N) are also reported^{31, 32}. Although NH_3 can be produced under milder conditions than conventional catalytic processes by using atomic state of N in Li_3N as N-source, regeneration of Li_3N from the stable by-products is difficult. If Li can be generated by reducing the products, Li_3N is easily formed by the reaction with N_2 because metallic state Li possesses high dissociation properties of N_2 molecule even at room temperature³². However, the Li generation from stable materials such as LiH and LiOH is thermodynamically difficult, and then more than 500 °C is necessary for the reduction. As a result, the above NH_3 synthesis systems consume materials or require complicated multi-step reactions by using high temperature and/or electrochemical processes for the Li_3N regeneration. It is

reported that Li alloys (Li_xM : $\text{M}=\text{C}, \text{Si}, \text{Ge}, \text{Sn}$) reversibly absorb and desorb N_2 below $550\text{ }^\circ\text{C}$ by following reaction³³,



The alloys are nitrogenated below $450\text{ }^\circ\text{C}$ to form low-composition Li alloys, and especially the nitrogenation of $\text{Li}_{22}\text{Sn}_5$ alloy proceed from around room temperature. The results suggest that Li in the alloys shows similar N_2 dissociation properties to the metallic Li. The Li_3N and M mixture prepared as ideal products react in wide temperature range $100\text{-}550\text{ }^\circ\text{C}$ to form Li alloys with N_2 desorption. The reaction temperature of the alloy formation is lower than the regeneration temperature of Li from Li_3N , which is higher than $600\text{ }^\circ\text{C}$. The reversible nitrogenation/denitrogenation of the Li alloy is based on the high N_2 dissociation properties and diffusivity of Li. The similar reversible reactions are found in the case of H_2 as follows,



The hydrogenation and dehydrogenation of all the systems can be operated below $500\text{ }^\circ\text{C}$ by destabilizing LiH by the reaction with M^{34} .

In this work, the pseudo catalytic process of NH_3 synthesis by using Li-Sn alloy is proposed, in which it is composed of the nitrogenation, NH_3 generation by reaction of the nitrogenated alloy with H_2 , and regeneration (reformation of initial alloy). The reaction properties of the Li-Sn alloy for each process are investigated by gas-switching experiments, and moreover the NH_3 generation properties via reaction between Li alloy and $\text{H}_2\text{-N}_2$ mixed gas.

Experiments

Lithium (Li, $99\geq\%$) and tin (Sn, 99.99%) were purchased from Sigma Aldrich and Kojundo Chemical Lab. as starting materials, respectively. To synthesize $\text{Li}_{17}\text{Sn}_4$, Li and Sn were weighed and mixed with a molar ratio of 17:4 (4.25:1). Then, the mixture was heat-treated at $500\text{ }^\circ\text{C}$ for 12 h with $5\text{ }^\circ\text{C}/\text{min}$ of heating rate under 0.1 MPa of Ar.

The following thermal reaction properties were investigated by thermogravimetry (TG) (Rigaku, TG8120),

which was placed into a grove box (Miwa MFG) filled with purified Ar (>99.9999%), and the generated gases were *in-situ* analyzed by mass spectroscopy (MS) (Canon Anelva Corporation, M-QA200TS). The nitrogenation of the Li-Sn alloy was performed under 0.1 MPa of N₂ with flow rate of 300 cm³/min at temperature range from room temperature to 500 °C with a heating rate of 5 °C/min. The nitrogenated Li-Sn alloy was heated up to 300 °C with heating rate of 5 °C/min under 0.1 MPa of H₂ with flow rate of 300 cm³/min to investigate the NH₃ generation properties. The heat treatment of products obtained by the above reactions with N₂ and H₂ was carried out under 0.1 MPa of Ar (inert gas) with flow rate of 300 cm³/min up to 500 °C with a heating rate of 5 °C/min. The above 3-steps processes were repeated 3 times to examine cyclic properties. In addition to the above gas-switching process, the conventional catalytic properties of Li alloys for the NH₃ synthesis process were investigated by the home-made gas flow type apparatus. The mixed gas of N₂ and H₂ with 1:3 molar ratio was used as flow gas with rate of 100 cm³/min (H₂: 75 cm³/min, N₂: 25 cm³/min), where the gas ratio was adjusted by mass flow controllers. The Li-Sn alloy was packed into the reactor made of SUS and heated to 500 °C by furnace. The qualitative and quantitative analyses of generated NH₃ was carried out by Fourier transform infra-red spectroscopy (FT-IR) with optical path length of 1.5 m (PerkinElmer, Frontier T+MCT NB). The reaction products were identified using the X-ray diffraction (XRD) measurements (Rigaku, RINT-2100, Cu K α radiation). In this procedure, the sample was put on a glass plate and covered by a polyimide sheet (Du Pont-Toray Co., Ltd., Kapton) in the grove box to avoid the oxidation of the sample. Transmission electron microscope (TEM) (JEOL, JEM-2010) equipped with energy dispersive spectroscopy (EDS) analyses was used to characterize the reaction products, and electron diffraction patterns were measured for the phase identification. To observe clear variation of sample by the nitrogenation, the Li-Sn alloy react with N₂ gas at a load lock chamber of lens barrel, and the TEM images were observed and compared before and after the nitrogenation.

Results and Discussion

Figure 1 shows TG-MS profiles of the Li-Sn alloy under N₂, H₂, and Ar flow, and Figure 2 shows XRD patterns of as-synthesized Li-Sn alloy and after the above reactions, where the broken line in Fig. 1 shows temperature program for each experiment. Main diffraction peaks observed in the XRD pattern of the as-synthesized Li-Sn alloy are assigned to Li₁₇Sn₄ (Li_{4.25}Sn) phase. To investigate the

reaction between $\text{Li}_{17}\text{Sn}_4$ and N_2 , the sample was heated up to 500 °C under 0.1 MPa N_2 flow as shown in Figure 1(a). Here, although the reactivity of Li-Sn alloy with N_2 gas around room temperature was examined, no weight change was observed.

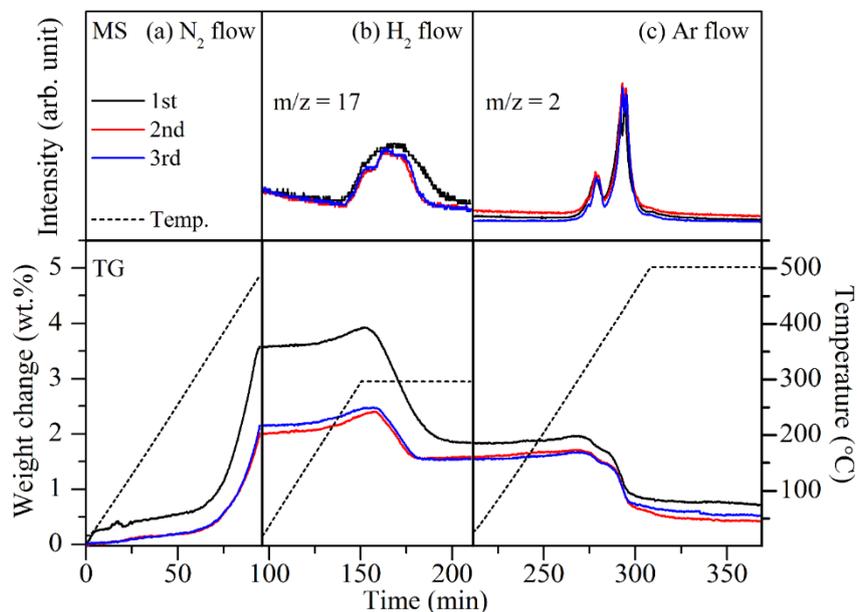


Figure 1 TG-MS profiles of $\text{Li}_{17}\text{Sn}_4$ under 0.1 MPa of (a) N_2 , (b) H_2 , and (c) Ar flow conditions.

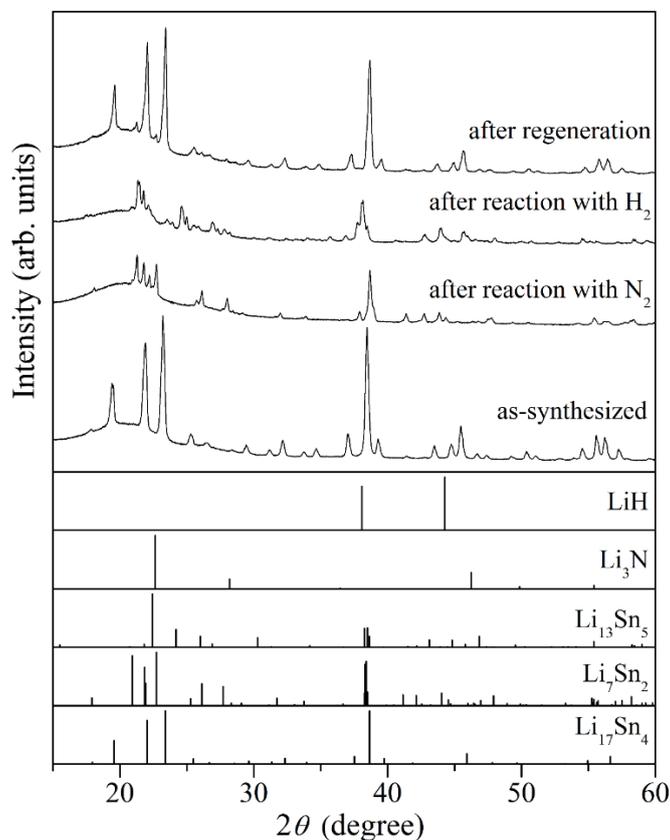


Figure 2 XRD patterns of the as-synthesized $\text{Li}_{17}\text{Sn}_4$ alloy and the products after the reactions.

The weight of the sample began to gradually increase when the heating program started, indicating that exothermic nitrogenation gradually proceeded around 50 °C. The reaction kinetics of nitrogenation is significantly changed around 400 °C due to the thermal activation. The XRD pattern of the sample after the reaction with N₂ corresponded to mainly Li₇Sn₂ (Li_{3.50}Sn) phase, and some small peaks were assigned to Li₁₃Sn₅ (Li_{2.60}Sn) phases. By the reaction with N₂, Li₁₇Sn₄ was converted into the alloys with lower Li concentration than starting alloy as follows,



It is expected that the nano-sized or amorphous Li₃N is formed as the reaction product because no other products are found in the XRD patterns. The weight gain estimated from the above equation is 2.4 wt.%. However, the value obtained from experiment was about 3.5 wt.%. The yield in excess of 100% would be caused by the coexistence of the lower Li composition phases such as Li₁₃Sn₅ than Li₇Sn₂ in the reaction product. In fact, it is reported that Li₂₂Sn₅ was converted into Li₁₃Sn₅ under 0.1 MPa N₂ pressure³³. To characterize the reaction process of the nitrogenation, quasi *in-situ* TEM observation for the nitrogenation of Li₁₇Sn₄ alloys was performed. TEM images, electron diffraction patterns, and results of EDS analysis are shown in Figure 3. The particle of as-synthesized Li₁₇Sn₄ showed clear edge as shown in Fig. 3(a). After the reaction with N₂ gas, the products with low contrast were observed at surface part of Li₁₇Sn₄ particle as shown in Fig. (b). In the diffraction patterns of the above particles of Fig. 3(c) and (d), Li₁₇Sn₄ and Li₇Sn₂ phases are found before and after the nitrogenation, respectively. This phase variation is consistent with the results of XRD measurements. Here, Li₂O was observed as impurity phase for both results. For the other particle, the observed TEM images and its variation are similar to the above first particle as shown in Fig. 3(e) and (f).

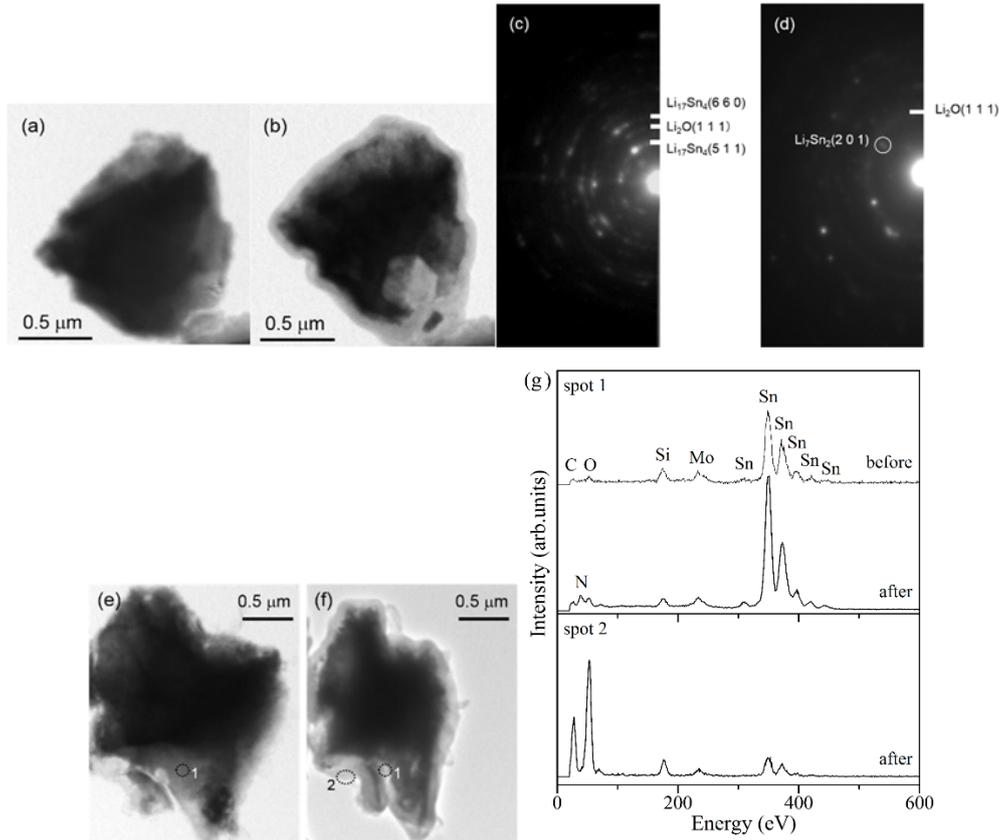


Figure. 3 TEM images of (a, e)the as-synthesized $\text{Li}_{17}\text{Sn}_4$, (b, f)the sample after nitrogenation, and (c, d) electron diffraction patterns, and (g) results of EDS analyses for spot 1-2 before and after the nitrogenation

The EDS analyses were carried out for spot 1 and 2 of particle shown in Fig. 3(f), and the results are shown in Fig. 3(g). No considerable amount of N atoms were observed at surface part of the products (spot 1) while the peak intensity corresponding to O atoms was higher. On the other hand, significant amount of N atoms exist at boundary area between Li-Sn alloy and products (high and low contrast parts) in EDS result of spot 2 after the nitrogenation while no peak corresponding to N was found before the reaction with N_2 . The TEM image observed after the nitrogenation is similar to previous results of the *ex-situ* nitrogenated Li-Sn alloy³³, indicating that the nano-sized Li_3N would be generated as products at surface part of the alloy particles. However, the generated Li_3N is very active and possibly react with tiny amount of O_2 , which might be contaminated in the experiments as impurity, to form stable Li_2O . In fact, Li_2O was observed by the electron diffraction measurements. Thus, the

TEM results in this work is able to be explained by the following processes. The Li-Sn alloy reacts with N₂ gas, and then nano-sized/amorphous Li₃N is generated as the product with low contrast near alloy surface due to Li diffusion from inside of alloy like electrode reaction of lithium ion battery. After that, the generated Li₃N is changed to Li₂O by the reaction with tiny O₂ as impurity because Li₃N is quite sensitive for oxidation³⁵. As a result, the above layered products are observed around the alloy particle.

The reaction between the nitrogenated Li-Sn alloy and H₂ gas was performed to synthesize NH₃. If Li₃N is formed during the above nitrogenation, NH₃ can be generated by the following equation³¹,



Fig. 1(b) shows TG-MS profiles of the nitrogenated alloy under 0.1 MPa of H₂ flow. The sample weight slightly increased from starting point of heating. The clear weight loss started from 300 °C, and then the MS signal corresponding to NH₃ ($m/z = 17$) was observed. It is suggested that the expected NH₃ synthesis reaction occurred. In addition, the Li₃N formation by the nitrogenation of alloy is indirectly clarified. From the XRD pattern of the products after the reaction with H₂ (Fig. 2), it is difficult to accurately identify the reaction products, however it is expected that the several Li-Sn phases with lower Li concentration such as Li₁₃Sn₅, Li₅Sn₂, Li₇Sn₃, and LiSn coexist. When only reaction between Li₃N and H₂ proceeds, the Li-Sn alloy phase is not changed. The structural changes and slight increase in sample weight below 300 °C indicate the direct hydrogenation of Li-Sn alloy simultaneously occurs with the NH₃ generation reaction. The diffraction peaks corresponding to LiH were not found because the generated amount is small, the diffraction intensity are essentially weak, and the peak positions are overlapped with those of Li₁₃Sn₅ and/or Li₇Sn₂ phases.

Fig. 1(c) shows TG-MS profiles under Ar flow conditions of the sample after the NH₃ synthesis. The weight of sample began to decrease at 350 °C with H₂ desorption, suggesting that the reaction between Li-Sn alloys and LiH proceeded. From the XRD pattern of the products after this reaction, the main observed peaks were assigned to Li₁₇Sn₄ although small peaks corresponding to the

Li-Sn alloy with other compositions were also observed. In other words, the starting phase $\text{Li}_{17}\text{Sn}_4$ can be regenerated below $350\text{ }^\circ\text{C}$ after the NH_3 synthesis. As shown in the TG result, the weight change is not reached to zero (starting weight) during the 3-steps process, indicating that about 0.8 wt.% of irreversible part also exists. Thus, the reaction conditions should be optimized to enhance the reversible parts.

The TG-MS results for 2nd and 3rd cycles for the NH_3 synthesis of the Li-Sn alloy are also shown in Fig. 1. For the nitrogenation, although the reactivity around room temperature is slightly lowered, the profile of the TG curve was almost similar to the 1st one. The weight gain by the reaction with N_2 was about 2 wt.%. The reaction temperature of NH_3 synthesis was $300\text{ }^\circ\text{C}$, which was same as that of the 1st cycle. The NH_3 generation amount was also decreased due to the decrease in the amount of nitrogenation. The TG-MS profiles due to the hydrogen desorption from the sample after the NH_3 synthesis for the 1st and 2nd cycles were almost consistent, where discussion of difference in the TG curves for the regeneration of alloy is essentially difficult because of low contribution of hydrogen for the sample weight. Although the synthesized amount of NH_3 is relatively decreased from 2nd cycle, the reactions of nitrogenation, NH_3 synthesis, and alloy regeneration become stable because results obtained in the 2nd and 3rd cycles are not clearly changed. The as-synthesized alloy has various active sites for the NH_3 synthesis process, and some parts are irreversible for the reaction conditions. However, the reversible parts stably react with high durability. The high reversibility would be caused by the characteristic reaction process of this system. As described above, Li dissociates N_2 and forms active nitride on the surface of alloy, indicating that the Li in alloy diffused from inside to surface parts. In the alloy regeneration process, Li located on the surface is diffused into inside and forms stable alloy phases again. Namely, it is expected that the pseudo-catalytic reactivity is preserved during the cycle because of the above reaction processes due to the Li extraction and insertion.

The Li-Sn alloy was heated up to $500\text{ }^\circ\text{C}$ under mixed gas of N_2 and H_2 flow conditions to investigate conventional catalytic properties, which is differently from the above “pseudo catalyst” process using the gas-switching. Fig. 4 shows the IR spectra of gas passed through the reactor packed

with Li-Sn alloy at different temperature. From about 380 °C, the absorption peaks corresponding to stretching vibration modes of NH₃ were observed. The higher amount of NH₃ is generated in the temperature range from 400-450 °C although the amount of generated NH₃ is gradually decreased at higher than 450 °C. These results indicate that suitable temperature window exist for the effective NH₃ synthesis. The FT-IR spectrum with the highest absorption peak of NH₃ observed at 412 °C was quantitatively analyzed by using calibration results obtained from the analyses of reference gas with different NH₃ concentration, which is NH₃ and Ar mixed gases. As a result, the NH₃ concentration generated by the reaction of Li-Sn alloy was about 400 ppm, which is ten times smaller than 4320 ppm estimated from thermodynamic equilibrium state at 400 °C. Thus, the NH₃ synthesis properties of Li-Sn alloy as conventional catalytic processes are poor.

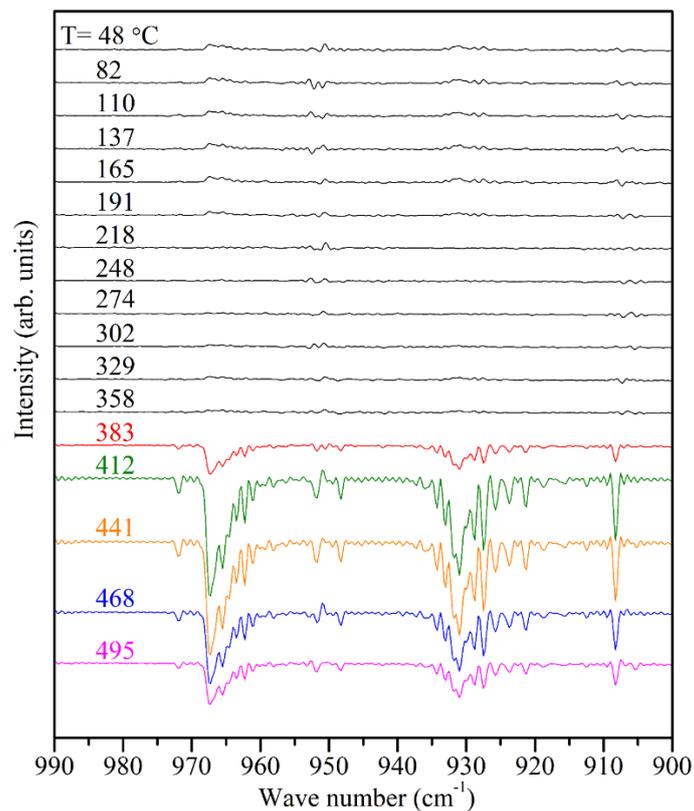


Figure 4 IR spectra of outlet gas from column with Li₁₇Sn₄ alloy at different temperature

From the above experimental results, it is recognized that the Li-Sn alloy is available as “pseudo catalyst” with high durability for NH₃ synthesis via gas-switching processes. By using this

process, NH_3 can be synthesized below 350 °C under 0.1 MPa.

Conclusion

In this work, Li-Sn alloy ($\text{Li}_{17}\text{Sn}_4$) is synthesized by thermochemical method at 500 °C. The nitrogenation properties was investigated using the TG measurements under N_2 gas flow. It is found that the reaction between $\text{Li}_{17}\text{Sn}_4$ and N_2 begins at room temperature and accelerated from around 400 °C. The products obtained by the nitrogenation process is mainly Li_7Sn_2 with lower Li concentration, suggesting that the Li atoms in the alloy reacts. Although Li_3N is not found in XRD patterns after the nitrogenation, it is indicated from TEM analyses that Li atoms is diffused from inside of alloy to surface part and forms nitride. The nitrogenated sample reacts with H_2 to form NH_3 at 300 °C under 0.1 MPa. After the NH_3 generation, the product can be recycled back to initial alloy phase $\text{Li}_{17}\text{Sn}_4$ around 350 °C. Therefore, by using the reaction of Li alloy as “pseudo catalysts”, NH_3 can be synthesized below 400 °C under 0.1 MPa. Interestingly, the reactivity is not drastically changed after cycles. This phenomena would be originated in the characteristic dynamics of Li atoms during the reaction process.

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