

Hydrogen storage of metal nitride by a mechanochemical reaction

Yoshitsugu Kojima* and Yasuaki Kawai

Toyota Central R&D Labs., Inc., Nagakute-cho, Aichi-gun, Aichi 480-1192, Japan.

E-mail: kojima@mosk.tytlabs.co.jp; Fax: +81-561-63-6137; Tel: +81-561-63-5367

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Metal imides (Li_2NH , CaNH), a metal amide (LiNH_2) and metal hydrides (LiH , CaH_2) were synthesized by ball milling of their respective metal nitrides (Li_3N , Ca_3N_2) in a H_2 atmosphere at 1 MPa and at room temperature.

Hydrogen (H_2) can be stored in tanks as compressed¹ or liquefied H_2 ¹ or by adsorption on carbon materials.^{1–6} It can also be stored in H_2 -absorbing alloys⁷ or as a chemical hydride, such as NaBH_4 ^{8,9} or NaAlH_4 ,¹⁰ as well as in an organic hydride, such as methylcyclohexane or decalin.¹¹ In recent years, attention has been given to metal nitrides.^{12,13} Chen *et al.* reported that metal nitride (Li_3N) absorbed hydrogen at high temperature (468–528 K).¹² For usable H_2 storage, H_2 absorption/desorption at ambient temperature is necessary and Ichikawa *et al.* demonstrated that a mixture of LiNH_2 and LiH prepared by a ball milling process lowered the temperature of H_2 desorption.¹³ Recently, it has been shown that chemical reaction can occur at room temperature during mechanochemical processing.^{14,15}

For the first time, we have demonstrated that metal imide, metal amide and metal hydride can be synthesized using a mechanochemical reaction of a metal nitride (Li_3N , Ca_3N_2) in a H_2 atmosphere at a pressure of 1 MPa and at room temperature. The starting materials for this mechanochemical reaction were lithium nitride (Li_3N) and calcium nitride (Ca_3N_2).† Mechanochemical reactions were performed in a planetary ball mill (Fritsch P-5). The mill container (Cr–Mo steel pot with an internal volume of 300 mL) was loaded with 5 g of metal nitride and 40 pieces of steel ball with a diameter of 9.5 mm. The metal nitrides were milled at 400 rpm for 20 h in a H_2 gas atmosphere at a pressure of 1 MPa at room temperature (296 K).

The products after ball milling were light brown, different from the dark brown starting materials (Fig. 1). The X-ray diffraction (XRD) intensity curves (Fig. 2) show the ball-milled Li_3N is a mixture which includes Li_3N , Li_2NH , LiNH_2 and LiH .¹⁶ The diffraction peaks of the ball-milled Li_3N at 2θ of 38.3° , 44.5° and 64.8° are raised from (111), (200) and (220) planes of LiH in which its unit cell is cubic in shape.¹⁶ The unit cell of Li_2NH is cubic in shape¹⁶ and the unit cell of LiNH_2 is tetragonal in shape.¹⁶ As the XRD curve of the LiNH_2 phase is quite similar to that of the Li_2NH phase, it is difficult to characterize the hydrogenating reaction during ball milling only from the XRD curves. The strongest peak of the ball milled Li_3N in the XRD curve is at about 33° , which comes from either Li_2O or LiOH . This contamination might originate from small leaks in the pulverizing system. The structure of the ball-milled Li_3N was also investigated by infrared spectroscopy. Fig. 3 shows the infrared absorption spectra of the ball-milled Li_3N , Li_3N , LiNH_2 (Sigma-Aldrich, purity: 95%) and Li_2NH . Li_2NH was synthesized by decomposing LiNH_2 at 673 K

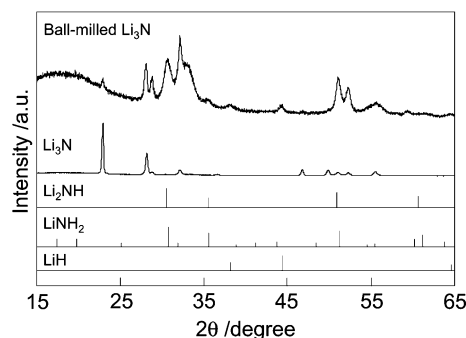
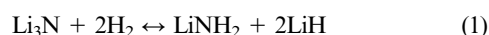


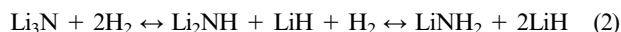
Fig. 2 X-ray diffraction intensity curves of ball-milled Li_3N in H_2 and Li_3N together with the data of LiH (JCPDS file No. 09-0189), Li_2NH (JCPDS file No. 06-0417) and LiNH_2 (JCPDS file No. 06-0418).

under vacuum (0.1 Pa) for 1 h.¹² The N–H symmetric and asymmetric stretching vibrations of LiNH_2 occur at 3260 cm^{-1} and 3315 cm^{-1} , respectively.¹⁷ Li_2NH gives rise to two characteristic bands at 3180 cm^{-1} and 3250 cm^{-1} . We notice that the ball-milled Li_3N contains Li_2NH and LiNH_2 due to the presence of these characteristic IR bands at 3180 cm^{-1} , 3260 cm^{-1} and 3315 cm^{-1} . Thus, we believe that the ball-milled Li_3N in H_2 is partially converted to Li_2NH , LiNH_2 and possibly LiH . The O–H stretching vibration of LiOH is not in this region. This suggests that from the XRD curve, the peak at about 33° is Li_2O .

It has been reported that hydrogen storage in Li_3N takes the following reaction path.¹²



H_2 of 10.4 wt% [$2\text{H}_2/\text{Li}_3\text{N} + 2\text{H}_2$] can be stored in this reaction. The H_2 content of the ball-milled Li_3N determined using the Hydrogen Analyzer was 5.0 wt% and half of the theoretical value. The H_2 storage involved the following two-step reaction path.¹²



We speculate that insufficient H_2 was supplied in Li_3N powder, thus unreacted Li_3N remained due to the decrease in the H_2 content during the ball milling.

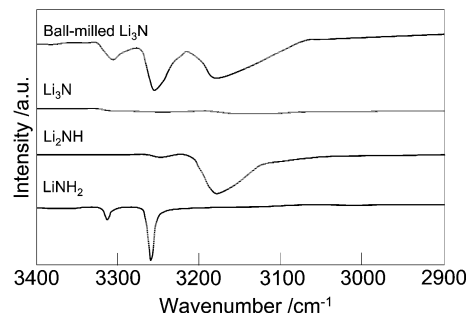


Fig. 3 Infrared absorption spectra of ball-milled Li_3N in H_2 and Li_3N together with the data of Li_2NH and LiNH_2 .

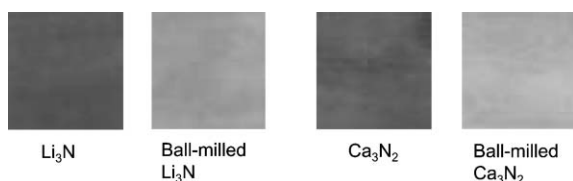


Fig. 1 Change of colour by mechanochemical reaction.

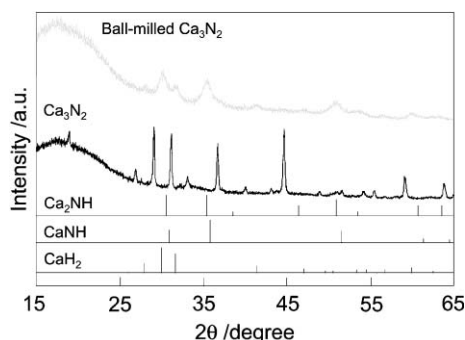


Fig. 4 X-ray diffraction intensity curves of ball-milled Ca_3N_2 in H_2 and Ca_3N_2 together with the data of CaH_2 (JCPDS file No. 65-2384), Ca_2NH (JCPDS file No. 26-0308) and CaNH (JCPDS file No. 75-0430).

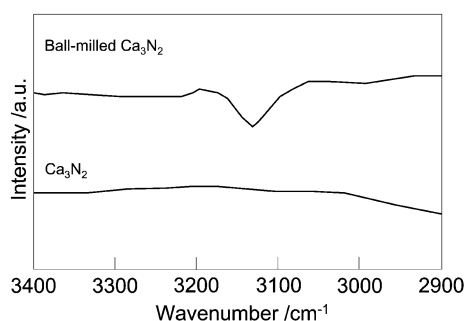
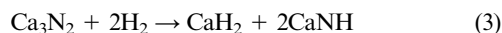


Fig. 5 Infrared absorption spectra of ball-milled Ca_3N_2 in H_2 and Ca_3N_2 .

The XRD intensity curves of ball-milled Ca_3N_2 , CaH_2 and Ca_2NH are shown in Fig. 4. Fig. 4 indicates that the ball-milled Ca_3N_2 in H_2 does not contain Ca_3N_2 . We notice that the diffraction peaks of the ball-milled Ca_3N_2 at 2θ of 27.9° , 30.1° , 31.8° , 41.5° and 60.0° are raised from (011), (200), (111), (211), (202) planes of CaH_2 , in which the unit cell of CaH_2 is orthorhombic in shape.¹³ The unit cells of Ca_2NH and CaNH are cubic in shape¹⁶ and their XRD curves are similar to each other.

The structure of the ball-milled Ca_3N_2 was also characterized by infrared spectroscopy. Fig. 5 shows the infrared absorption spectra of the ball-milled specimen in comparison to commercial Ca_3N_2 . The ball-milled specimen now contains a stretch at 3130 cm^{-1} , which is due to the presence of CaNH or Ca_2NH . The crystal structure of CaNH generated from XRD indicates the presence of an N–H bond, but the crystal structure generated by XRD shows that Ca_2NH does not have the bond. Thus, we found that the ball-milled Ca_3N_2 includes CaNH . The H_2 content of the ball-milled Ca_3N_2 examined using the Hydrogen Analyzer was 3.2 wt%. A very small amount of ammonia was detected using a gas detector tube ($4 \times 10^{-7}\text{ g NH}_3/\text{g ball-milled Ca}_3\text{N}_2$) in the ball-milled Ca_3N_2 . Therefore, the major reaction of Ca_3N_2 and H_2 by the mechanochemical reaction can be expressed by equation (3)



where the theoretical H_2 content obtained by equation (3) is 3.1 wt% [$2\text{H}_2/(\text{CaH}_2 + 2\text{CaNH})$]. The H_2 absorption during milling suggests that the hydrogenation process is a two-step

process as follows. H_2 is firstly absorbed on new particle surfaces created by pulverization during initial milling. The absorbed H_2 reacts with metal nitride to form metal imide, metal amide and metal hydride under further high-energy ball impacts. Local temperature rise, induced by ball impacts, may also contribute to the hydrogenation reaction.

In conclusion, mixtures of metal imide, amide, hydride (Li_2NH , LiNH_2 , LiH or CaNH , CaH_2) can be synthesized by a mechanochemical reaction of their respective metal nitride (Li_3N , Ca_3N_2) in a H_2 atmosphere at room temperature. The H_2 contents of the ball-milled Li_3N and Ca_3N_2 were 5.0 and 3.2 wt%, respectively.

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Notes and references

† Li_3N (Kojundo Chemical Laboratory Co., Ltd., Japan, molecular weight: 34.82, density: 1.38 g cm^{-3} , purity: > 99%) and Ca_3N_2 (Sigma-Aldrich, molecular weight: 148.25, density: 2.63 g cm^{-3} , purity: > 99%) were used in this experiment. High purity H_2 gas (> 99.99999%) was used as the reaction atmosphere. A Thermo Nicolet AVATAR 360 E.S.P. FT-IR spectrometer with an ATR system was used for IR studies in the wavenumber region from 3400 to 2900 cm^{-1} in an inert atmosphere of N_2 . X-ray diffraction intensity curves in an inert atmosphere (Ar) were recorded with $\text{CuK}\alpha$ radiation (50 kV, 300 mA) filtered by a monochromator using Rigaku Rint-TTR. The apertures of the first, second and third slits were 0.5, 0.5 and 0.15 mm, respectively. With the Horiba EMGA-621 Hydrogen Analyzer, H_2 contained in a specimen was extracted by heating at 2273 K in an inert gas (Ar). After column separation, H_2 was quickly analysed with a thermal conductivity detector.

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