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Hydrogen storage of metal nitride by a mechanochemical reaction

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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 compressed[1] or liquefied H_2[1] or by adsorption on carbon materials.[1–6] It can also be stored in H_2-absorbing alloys[7] 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 shape[16] 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 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.

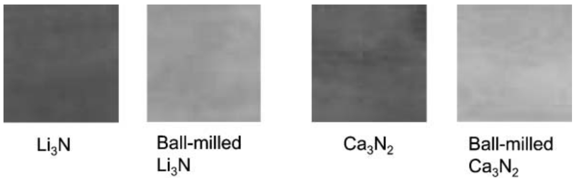

Fig. 1 Change of colour by mechanochemical reaction.

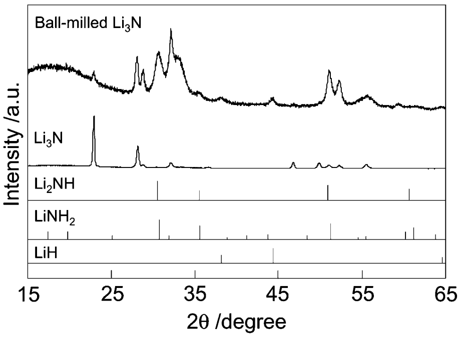

Fig. 2 X-ray diffraction intensity curves of ball-milled Li_3N in H_2 and Li_3N together with the data of LiH (JCPDS file No. 09-0189), Li_2NH (JCPDS file No. 06-0417) and $LiNH_2$ (JCPDS file No. 06-0418).

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

$$Li_3N + 2H_2 \leftrightarrow LiNH_2 + 2LiH \quad (1)$$

H_2 of 10.4 wt% [$2H_2/Li_3N + 2H_2$] 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]

$$Li_3N + 2H_2 \leftrightarrow Li_2NH + LiH + H_2 \leftrightarrow LiNH_2 + 2LiH \quad (2)$$

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.

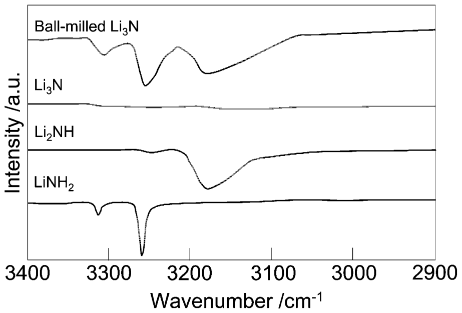

Fig. 3 Infrared absorption spectra of ball-milled Li_3N in H_2 and Li_3N together with the data of Li_2NH and $LiNH_2$.

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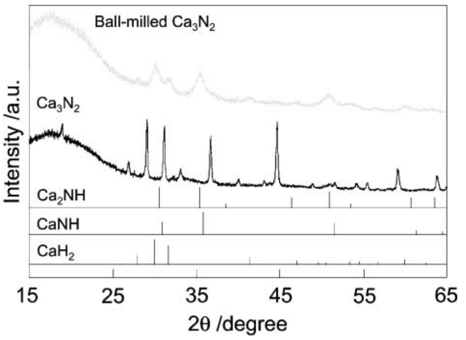

Fig. 4 X-ray diffraction intensity curves of ball-milled Ca_3N_2 in H_2 and Ca_3N_2 together with the data of CaH_2 (JCPDS file No. 65-2384), Ca_2NH (JCPDS file No. 26-0308) and CaNH (JCPDS file No. 75-0430).

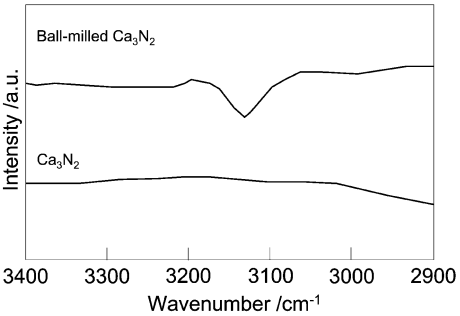

Fig. 5 Infrared absorption spectra of ball-milled Ca_3N_2 in H_2 and Ca_3N_2.

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 shape[16] 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 (4×10^{-7} g NH_3/g ball-milled Ca_3N_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)

$$Ca_3N_2 + 2H_2 \rightarrow CaH_2 + 2CaNH \qquad (3)$$

where the theoretical H_2 content obtained by equation (3) is 3.1 wt% [$2H_2/(CaH_2 + 2CaNH)$]. 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 ThermoNicolet 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 CuKα 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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