



HOKKAIDO UNIVERSITY

Title	Hydrogen absorption/desorption properties of light metal hydroxide systems
Author(s)	Tanaka, Fuga; Nakagawa, Yuki; Isobe, Shigehito et al.
Citation	International Journal of Energy Research, 44(4), 2941-2951 https://doi.org/10.1002/er.5113
Issue Date	2020-03-25
Doc URL	https://hdl.handle.net/2115/80654
Rights	This is the peer reviewed version of the following article: Tanaka, F, Nakagawa, Y, Isobe, S, Hashimoto, N. Hydrogen absorption/desorption properties of light metal hydroxide systems. Int J Energy Res. 2020; 44: 2941- 2951., which has been published in final form at https://doi.org/10.1002/er.5113 . This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions.
Type	journal article
File Information	manuscript_tanaka.pdf



Hydrogen ab/desorption properties of light metal hydroxide systems

Fuga Tanaka¹ Yuki Nakagawa² Shigehito Isobe² Naoyuki Hashimoto²

Summary

In light metal hydroxide systems, hydrogen desorption generally occurs in exothermic reactions, therefore these reactions are irreversible in principle. However, according to theoretical calculation of thermodynamics, some of these systems can desorb hydrogen in endothermic reactions. In this research, several hydroxide systems were studied to clarify the reversibility of these systems. Six types of hydroxide systems ($XH + Y(OH)_n$, X : Li, Na, Y : Li, Na, Mg) were prepared by ball milling, then the desorption properties of these systems were evaluated. As a result, NaH + LiOH and NaH + NaOH systems desorbed hydrogen in endothermic reactions. Also, NaH + NaOH system absorbed hydrogen almost 100% reversibly under 300 °C and 1.0 MPa H₂ pressure. The reversibility in NaH + LiOH system was not accomplished in our experimental condition, because high pressure of GPa order is required for the rehydrogenation. In order to modify the desorption kinetics, we added KH catalyst to NaH + LiOH and NaH + NaOH systems. The hydrogen desorption temperature of the two systems was decreased by addition of 1 mol% of KH. The catalytic effect on hydrogen desorption properties was sustained even after the rehydrogenation of KH-added NaH + NaOH system.

KEYWORDS

hydrogen storage • dehydrogenation • hydrogenation • light metal hydroxide • potassium

1 INTRODUCTION

1.1 Light metal complex hydride systems

To realize hydrogen energy system, it is necessary to establish the technology to store hydrogen safely. Storing hydrogen using metal hydride is one of the promising ways. It is desirable for hydrogen storage materials to be light and compact, therefore light metal hydride systems have been focused on.^{1,2} Among them, M-B-H and M-N-H systems have been reported a lot (M: light metal). For instance, metal borohydrides have high gravimetric and volumetric densities of H₂. The characterization of ab/desorption products and the kinetics enhancement by additive has been the subject-matter of investigations.³⁻⁵ A representative example of M-N-H systems is Lithium-Nitrogen-Hydrogen (Li-N-H) system. Li-N-H system has been reported a lot so far,^{6,7} however, this system has high value of enthalpy change and desorbs hydrogen at high temperature of around 300 °C. By contrast, Li-Mg-N-H system has some merits of having low value of enthalpy change and lower temperature of around 180 °C for hydrogen ab/desorption.⁸ The overall reaction of Li-Mg-N-H system is described as follows.⁸



¹Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

²Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan

Correspondence

Yuki Nakagawa, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan.

E-mail: y-nakagawa@eng.hokudai.ac.jp

In this study, M-O-H systems, which are composed of light metal and O (non-metal element in the second cycle on periodic table same as N or B), were focused on. Although the H₂ generation system using sodium hydroxide solution and silicon powder was reported in the previous study,⁹ the present study investigated the solid-solid reactions between hydrides and hydroxides. It is well known that hydrides mixed with hydroxides desorb hydrogen in lower temperature than those without hydroxides.¹⁰ Therefore, in this study, some systems with combination of light metal hydrides and light metal hydroxides were prepared and hydrogen ab/desorption properties of these systems were investigated.

1.2 Light metal hydroxide systems

In the hydroxide systems, thermodynamically stable oxides are generally formed after hydrogen desorption. Therefore, in hydroxide systems, hydrogen desorption generally occur in exothermic reactions and these reactions are irreversible in principle. This was the main cause why hydroxides systems have not been reported much. However, depending on the combination of hydroxide and hydride, there are some systems which can desorb hydrogen in endothermic reactions according to theoretical calculation of thermodynamics. For example, NaH + NaOH system desorbs hydrogen in endothermic reaction and absorb hydrogen reversibly through the following reaction.¹¹⁻¹³



In this study, reaction formulas of hydrogen desorption in six types of light metal hydroxide systems, which are composed of two types of light metal hydrides (LiH and NaH) and three types of light metal hydroxides (LiOH, NaOH and Mg(OH)₂), were predicted and standard enthalpy change (T = 298 K) for hydrogen desorption were calculated by using thermodynamic database¹⁴ as follows. In that case, we assumed that only oxides were formed after hydrogen desorption.



$$6.27 \text{ wt\% H}_2, \Delta H^\circ = -22.5 \text{ kJ/mol H}_2$$



$$4.20 \text{ wt\% H}_2, \Delta H^\circ = 9.9 \text{ kJ/mol H}_2$$



$$5.39 \text{ wt\% H}_2, \Delta H^\circ = -47.0 \text{ kJ/mol H}_2$$



$$4.20 \text{ wt\% H}_2, \Delta H^\circ = 34.4 \text{ kJ/mol H}_2$$



$$3.12 \text{ wt\% H}_2, \Delta H^\circ = 67.3 \text{ kJ/mol H}_2$$



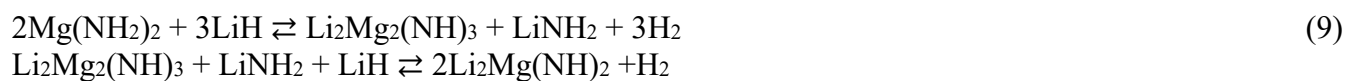
$$3.79 \text{ wt\% H}_2, \Delta H^\circ = 10.4 \text{ kJ/mol H}_2$$

As described above, LiH + NaOH, NaH + LiOH, NaH + NaOH, NaH + Mg(OH)₂ systems are predicted to desorb hydrogen in endothermic reactions. Theoretical hydrogen weight loss from each equation was also described as above. In this study, six types of light metal hydroxide systems (XH + Y(OH)_n, X: Li, Na, Y: Li, Na, Mg) were prepared and the hydrogen ab/desorption properties of them were evaluated.

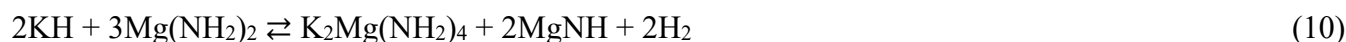
1.3 Catalytic effect of KH

To put into practical use of hydrogen storage materials, it is necessary to develop materials that desorb hydrogen in lower temperature, therefore the systems with various catalysts have been studied a lot. It is reported that Mg(NH₂)₂ / 2LiH system desorb hydrogen in lower temperature with addition of KH.^{15,16} By introducing KH (3 mol%) in the system, about 5 wt% of hydrogen can be reversibly desorbed and absorbed at about 107 °C.¹⁵ In this system, KH reacts with LiH or Mg(NH₂)₂ and some intermediates

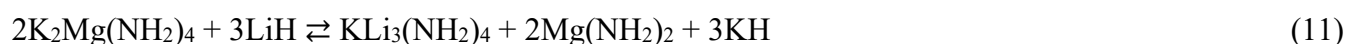
species containing K is formed. Dehydrogenation of $\text{Mg}(\text{NH}_2)_2$ / 2LiH system is a two-step reaction described as follows.¹⁶



In $\text{Mg}(\text{NH}_2)_2$ / 2LiH system with KH, $\text{Mg}(\text{NH}_2)_2$ firstly reacts with KH to form intermediate $\text{K}_2\text{Mg}(\text{NH}_2)_4$ as follows.¹⁶



Compared with those in $\text{Mg}(\text{NH}_2)_2$, some N-H bonds in $\text{K}_2\text{Mg}(\text{NH}_2)_4$ are much weaker, which facilitates its further interaction with LiH to generate $\text{KLi}_3(\text{NH}_2)_4$ as follows.¹⁶



The circular transformation among these species of KH, $\text{K}_2\text{Mg}(\text{NH}_2)_4$, and $\text{KLi}_3(\text{NH}_2)_4$ creates a more energy-favorable route for dehydrogenation, which results in the kinetic enhancement.¹⁶ The KH catalyst is also effective for LiNH_2 / LiH system. The activation energy for H_2 desorption was decreased by ~13% by the addition of 5 mol% KH.¹⁷ In the case of three-component $\text{Mg}(\text{NH}_2)_2$ / LiNH_2 / 4LiH system, a number of additives were added, among which only KH (3 wt%) greatly reduces the onset desorption temperature to below 90 °C.¹⁸ In this study, catalytic effect of KH on light metal hydroxide systems were also investigated.

2 MATERIALS AND METHODS

2.1 Preparation of metal hydroxide systems

Two types of light metal hydrides, LiH (95%) and NaH (95%), and three types of light metal hydroxides, LiOH ($\geq 98\%$), NaOH (97%) and $\text{Mg}(\text{OH})_2$ (95%), were purchased from Sigma-Aldrich. Then, six types of light metal hydroxide systems ($\text{XH} + \text{Y}(\text{OH})_n$, X: Li, Na, Y: Li, Na, Mg) were prepared by ball-milling method. These samples were milled under Ar gas atmosphere (0.1 MPa pressure) at 200 rpm for 60 min on a planetary ball-mill equipment, Fritsch P7. The molar ratio between hydride and hydroxide in equation (3)-(8) was basically applied for the experiments. The ratio for each system was described in the caption of each figure. To inhibit heat accumulation in the jar, samples were milled for 10 min in one direction, then paused for 5 min. The weight ratio of balls to samples was about 20 : 1. In order to avoid air exposure, all the samples handlings were conducted in a glove box filled with Ar.

2.2 Preparation of KH

KH was prepared by hydrogenation of K (99.95%), which was purchased from Sigma-Aldrich. Potassium (K) was hydrogenated under H_2 gas atmosphere (1.0 MPa pressure) at 650 °C for 30 h. The prepared sample was just identified as KH by XRD (Figure S1).

2.3 Analytical methods

Hydrogen desorption properties of six types of samples were analyzed on thermogravimetric analysis (TG), differential thermal analysis (DTA) and mass spectrometer (MS) combined system (using Bruker 2000SA for TG-DTA and ULVAC BGM-102 for MS). The samples were loaded in an alumina crucible and heated up to 400 °C at a rate of 5 °C/min under He flow. We detected not only H_2 ($m/z = 2$) but also H_2O ($m/z = 18$) in the MS experiment. However, H_2O desorption was not observed in all experiments. Therefore, hydrogen desorption amount was estimated by the weight loss from TG. These analyses were also conducted in a glove box filled with Ar to avoid air exposure.

XRD measurements (PHILIPS • X'Pert Pro • Cu K α radiation) were conducted in order to identify each crystalline phases of samples before and after hydrogen desorption. After that, the reaction formulas

for the hydrogen desorption of six types were derived based on the XRD results. The samples for XRD measurements were placed on a greased glass plate in a glove box and then sealed with a polyimide sheet to avoid air exposure. Microstructures of samples were observed by field emission scanning electron microscope (FE-SEM, JEOL JSM-7001FA). In order to minimize the air-exposure time, the samples were set on the specimen holder in the Ar-filled glovebox, and then transferred to the SEM chamber quickly.

Hydrogenation experiment was conducted under H₂ gas atmosphere (1.0 MPa pressure) for 30 hours. The hydrogenation temperature was set to 230 °C for NaH + LiOH system and 300 °C for NaH + NaOH system.

3 RESULTS AND DISCUSSION

3.1 Hydrogen desorption properties

3.1.1 LiH+LiOH

Figure 1 shows TG-DTA-MS profiles of LiH + LiOH with 1 : 1 molar ratio. It shows exothermic hydrogen desorption in the range of 200 °C–330 °C. To derive reaction formula of this hydrogen desorption, XRD was conducted (Figure 1). From the result of after milling (Figure 1 (a)), peaks of LiH and LiOH were observed, and after heating to 400 °C (Figure 1(b)), peaks of Li₂O were observed. Therefore, reaction formula of this system is described as follows.



Hydrogen weight loss from TG was similar to the theoretical value of 6.27 wt% as above. This reaction formula corresponds to the reported one.^{19–21}

3.1.2 NaH+LiOH

Two kinds of molar ratios were investigated for NaH + LiOH system. Figure 2 shows TG-DTA-MS profiles of NaH + LiOH with 1 : 2 molar ratio. It shows endothermic hydrogen desorption around 220 °C. From XRD result of NaH + LiOH after milling (Figure 2(a)), peaks of NaH and LiOH were observed, and after heating to 400 °C, peaks of Li₂O and NaOH were observed (Figure 2(b)). Therefore, reaction formula of this system is described as follows.



Weight loss from TG (2.6 %) was consistent with the above theoretical value.

Figure S2 shows TG-DTA-MS profiles of NaH + LiOH with 1 : 1 molar ratio. An endothermic reaction around 225 °C corresponds to the reaction (12), which is the same as in the case of 1 : 2 ratio. Figure S2(a)–(d) shows the XRD profiles. After the reaction (12), the remaining NaH reacted with NaOH to form Na₂O (Figure S2(c) and (d)) as follows.



The detailed desorption process of the reaction (7) is shown in the section of NaH + NaOH system. Total hydrogen desorption reaction of the system with 1 : 1 ratio can be described as the summation formula of reaction (12) and (7), that is reaction (6). In the Introduction part, we predicted reaction (6) would occur in a single step. However, NaH was changed to NaOH, but not to Na₂O. ΔH° of NaOH is -425.6 kJ/mol, whereas ΔH° of Na₂O is -414.6 kJ/mol.¹⁴ Therefore, thermodynamically stable NaOH was formed instead of Na₂O in the first desorption reaction.

3.1.3 LiH+NaOH

Figure 3 shows TG-DTA-MS profiles of LiH + NaOH with 1 : 1 molar ratio. It shows plural peaks of hydrogen desorption. An exothermic hydrogen desorption peak was observed at 196 °C. In addition, the peaks at 234 °C, 283 °C and 310 °C show endothermic hydrogen desorption reactions. Since this system desorbed hydrogen in multistage, XRD was conducted for the sample after milling and after each hydrogen desorption step (Figure 3(a)-(e)). After milling (Figure 3(a)), LiH and NaOH were observed. After heating to 208 °C (Figure 3(b)), XRD peaks show the phases of Li₂O and NaH in addition to LiH and NaOH. From the above, an exothermic hydrogen desorption at 196 °C shows a single reaction as follows.



This reaction formula corresponds to the reported one.²¹ From XRD result after heating to 262 °C (Figure 3(c)), peaks of LiH, Li₂O, NaH, NaOH and Na₂O were observed. Compared with Figure 3(b), peak intensity of Li₂O became stronger and new peak of Na₂O appeared in Figure 3(c). After heating to 287 °C (Figure 3(d)), peak intensity of Na₂O became stronger, but the intensity of NaOH became weaker. After heating to 400 °C (Figure 3(e)), the primary crystalline phases were Na₂O and Li₂O. According to the equation (13), NaH was formed after the exothermic hydrogen desorption step. Thus, the reaction between NaH and NaOH (reaction (7)) would form Na₂O. However, the XRD peak intensity of Li₂O was also increased by endothermic hydrogen desorption reactions in Figure 3. Thus, the endothermic hydrogen desorption reaction between LiH and NaOH (reaction (4)) could also occur. Further study will be needed in order to clarify the each hydrogen desorption step in this system.

3.1.4 NaH+NaOH

Figure 4 shows TG-DTA-MS profiles of NaH + NaOH with 1 : 1 molar ratio. It shows endothermic peaks of hydrogen desorption. From XRD result of after milling (Figure 4(a)), peaks of NaH and NaOH were observed, and after heating to 400 °C (Figure 4(b)), Na₂O was formed. Therefore, reaction formula of this system is described as follows.



Weight loss from TG (2.4 %) was a little smaller than the above theoretical value, which would originate from the unreacted NaOH as shown in Figure 4(b). This reaction formula corresponds to the reported one.¹¹⁻¹³

In the previous study, NaOH shows phase transition at 293 °C followed by melting at 319 °C.^{12,22} Therefore, the endothermic peak around 290 °C can be assigned to the phase transition of NaOH. Also, NaOH was changed to liquid state around 300 °C. Thus, we consider that solid-liquid reaction would occur in the second hydrogen desorption reaction (300-340 °C). This may be the reason why peak intensity of second hydrogen desorption was dominant. On the other hand, the first hydrogen desorption (200-290 °C) would be solid-solid reaction.

3.1.5 LiH+Mg(OH)₂

Figure 5 shows TG-DTA-MS profiles of LiH + Mg(OH)₂ with 2 : 1 molar ratio. It shows exothermic peaks of hydrogen desorption. Two hydrogen desorption peaks were observed in DTA and MS profiles. From XRD result of after milling (Figure 5(a)), peaks of LiH and Mg(OH)₂ were observed. After heating to 270 °C, the formation of intermediate phase of LiOH was observed (Figure 5(b)). Therefore, reaction formula in the first step can be described as follows.



The DTA and MS profiles in the latter step were similar to those of LiH + LiOH system (Figure 1). Actually, after heating to 400 °C (Figure 5(c)), the relative peak intensity of Li₂O became stronger than that of MgO. In addition, the peaks of LiH and LiOH were disappeared. Therefore, reaction formula in the second step is described as follows.



Hence, total hydrogen desorption reaction of LiH + Mg(OH)₂ system is the summation formula of reaction (14) and (3), that is reaction (5). Weight loss from TG (5.2 %) was consistent with the theoretical value of 5.39 % in reaction (5). This reaction formula corresponds to the reported one.²³

3.1.6 NaH+Mg(OH)₂

Figure 6 shows TG-DTA-MS profiles of NaH + Mg(OH)₂ with 2 : 1 molar ratio. From the results, hydrogen desorption of the first step (206 °C) shows an exothermic peak, and the second and third steps (252 °C and 292 °C) show endothermic peaks. From XRD result of after milling (Figure 6(a)), NaH and Mg(OH)₂ were observed and NaOH and MgO were formed after heating to 228 °C (Figure 6(b)). Therefore, the first step of hydrogen desorption is described as follows.



In this system, NaH changed to NaOH, but not to Na₂O. The reason of this phenomenon would be the same as NaH + LiOH system. After heating to 270 °C and 400 °C, peaks of NaH and NaOH got weaker and peaks of Na₂O were observed (Figure 6(c) and (d)). Therefore, the second and the third step can be described as follows.



This reaction occurred between unreacted NaH and the formed NaOH in reaction (15).

Total hydrogen desorption reaction of the NaH + Mg(OH)₂ system can be described as the summation formula of reaction (15) and (7), that is reaction (8). Weight loss from TG (2.9 %) was a little smaller than the theoretical value of 3.79 % in reaction (8), which would come from unreacted NaOH as shown in Fig. 6(d). We predicted reaction (8) would occur in a single endothermic step. However, in fact, the system desorbed hydrogen in an exothermic reaction in the first step (reaction (15)). Therefore, the rehydrogenation reaction of this system is difficult to occur according to thermodynamic principle.

3.2 Hydrogen absorption properties

From the investigation of hydrogen desorption properties, NaH + LiOH and NaH + NaOH systems desorbed hydrogen in endothermic reactions. Hence, we investigated hydrogen absorption properties of these systems. As shown in MS profile of Figure 7 (red line), hydrogen desorption was clearly observed from NaH + NaOH after rehydrogenation treatment. Therefore, it is confirmed that NaH + NaOH system can absorb hydrogen after the first desorption. Also, the MS profile after rehydrogenation was similar to that of the first desorption. The endothermic peak around 180 °C in DTA profile was only observed after rehydrogenation, which could originate from the formation of NaH-NaOH solid solution as shown in the previous study.^{19,24} From TG profiles of Figure 7, weight loss of the sample after rehydrogenation was almost the same value as that of NaH + NaOH sample, indicating the hydrogen desorption amount from rehydrogenated sample kept the same value as that of the first milled sample.

Figure 7(a) shows XRD profiles of sample after rehydrogenation. After hydrogen desorption, Na₂O was formed in NaH + NaOH system. However, Na₂O peaks were not observed after rehydrogenated sample and only peaks of NaH and NaOH were observed. Figure 7(b) shows the XRD profiles of milled NaH + NaOH system for comparison.

From the above, in this system, it is confirmed that Na₂O can absorb hydrogen reversibly about 100% to form NaH and NaOH. Also, this system can desorb hydrogen about 100% after rehydrogenation. These results correspond to the reported results.¹¹⁻¹³

In NaH + LiOH system with 1 : 2 molar ratio, hydrogen desorption was not observed after rehydrogenation treatment (Figure S3). In this system, NaOH and Li₂O phases were observed after H₂ desorption. Therefore, NaOH + Li₂O composite could not absorb hydrogen. From the van't Hoff equation as follows, the equilibrium dissociation H₂ pressure of these system is derived.

$$\ln(p/p^0) = \Delta H^\circ/RT - \Delta S^\circ/R \quad (16)$$

p : equilibrium dissociation pressure of hydrogen

p^0 : standard pressure

T : absolute temperature

R : gas constant

ΔH° : change of standard enthalpy

ΔS° : change of standard entropy

Applying the conditions of rehydrogenation experiment (NaH + LiOH: $T = 230^\circ\text{C}$), the equilibrium dissociation pressure of NaH+LiOH system with 1 : 2 molar ratio (the reverse process of reaction (12)) are derived as follows.

$$p \doteq 99 \text{ GPa}$$

In this paper, rehydrogenation experiment was conducted under 1.0 MPa of hydrogen pressure. This is the reason why rehydrogenation was not occurred. Therefore, high pressure of GPa order would be needed to rehydrogenate this system.

3.3 Particle Morphologies observed by SEM

Particle morphologies of pristine hydrides/hydroxides and NaH+NaOH composites were observed by SEM. Figure 8 shows SEM images of pristine NaH, NaOH and ball-milled NaH+NaOH composites. The size of pristine NaH particle was 10-30 μm and the size of NaOH particle was a little larger than NaH. It is interesting to note that the surface morphologies of pristine NaH and NaOH particles were bumpy. On the other hand, pristine LiH, LiOH and Mg(OH)₂ particles have a relatively smooth surface as shown in Figure S4. By ball-milling of NaH and NaOH, a lot of refined particles with the size of a few microns were observed. Also, the surface morphologies of some particles were changed to relatively smooth surface as shown in Figure 8(c), and others were bumpy like Figure 8(a) and (b). In order to clarify the detailed reaction process, further studies on the morphologies of composites would be useful.

3.4 Catalytic effect of KH on hydroxide systems

Figure 9(a) and 9(b) show MS profiles of 1mol% KH-added NaH + LiOH and NaH + NaOH systems, respectively. It is revealed that KH has catalytic effect on these systems and hydrogen desorption temperature was decreased, especially for NaH + NaOH system. Although two hydrogen desorption steps were observed in NaH + NaOH system without KH as shown in the previous section, KH-added system desorbed H₂ in one step below 300 $^\circ\text{C}$ as shown in the red line in Figure 9(b). In order to clarify the origin of kinetics improvement, activation energy for H₂ desorption reaction was estimated by using Kissinger

equation ($\ln(c/T_p^2) = -E_a/RT_p + \ln(RA/E_a)$, E_a : activation energy, c : heating rate, T_p : peak temperature, R : gas constant, A : frequency factor). Figure 10 shows the Kissinger plots. In the NaH + NaOH composite, the peak temperature of the first peak (corresponding to the solid-solid reaction) was used. The obtained activation energy was 114.8 kJ/mol for NaH + NaOH and 93.1 kJ/mol for KH-added NaH + NaOH, respectively. Thus, the decline in the activation energy barrier would be one of the important factor for the kinetics improvement.

Rehydrogenation experiment was conducted for NaH + NaOH + 1 mol% KH sample. The blue dashed line in Figure 9(b) shows hydrogen desorption of the sample after rehydrogenation. The hydrogen desorption temperature was similar to that of KH-added system (red line). From the above, it is revealed that the catalytic effect of KH was sustained even after rehydrogenation. Although the mechanism of catalysis has not been clarified yet, this study first demonstrated the positive effect of KH addition on hydroxide systems.

4 CONCLUSION

In this study, hydrogen ab/desorption properties of six types of light metal hydroxide systems ($XH + Y(OH)_n$, X : Li, Na, Y : Li, Na, Mg), and catalytic effect of KH on these systems were evaluated. NaH + LiOH and NaH + NaOH systems desorbed hydrogen in endothermic reactions, and LiH + LiOH, LiH + NaOH, LiH + $Mg(OH)_2$ and NaH + $Mg(OH)_2$ systems desorbed hydrogen in exothermic reactions. Endothermic hydrogen desorption reactions could also exist in LiH + NaOH system. In NaH + LiOH and NaH + $Mg(OH)_2$ systems, an intermediate phase of NaOH was formed, followed by a desorption reaction with NaH. In LiH + $Mg(OH)_2$ system, an intermediate phase of LiOH was formed, followed by a desorption reaction with LiH. In LiH + NaOH system, an intermediate phase of NaH was observed. NaH + NaOH system absorbed hydrogen reversibly almost 100% under the moderate condition of 300 °C and 1.0 MPa H_2 pressure. In NaH + LiOH system, high pressure of GPa order is needed for rehydrogenation. With addition of 1 mol% of KH, hydrogen desorption temperature of NaH + LiOH and NaH + NaOH system was decreased. The KH catalytic effect on hydrogen desorption properties was sustained even after the rehydrogenation treatment of KH-added NaH + NaOH system.

ACKNOWLEDGEMENTS

This work was supported by JSPS KAKENHI Grant Number JP17K14827. A part of this work was conducted as High-voltage Electron Microscope Laboratory in Hokkaido University, supported by “Nanotechnology Platform” and “Microscopic Analysis for Nano-materials Science and Bio-Science Open Unit (MANBOU)” program of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. The authors thank Mr. N. Noto for his help in the TG-DTA-MS experiments.

ORCID

Yuki Nakagawa <https://orcid.org/0000-0001-5020-1458>

Shigehito Isobe <https://orcid.org/0000-0003-3824-5575>

REFERENCES

- 1 Ley MB, Jepsen LH, Lee YS, Cho YW, Bellosta von Colbe JM, Dornheim M, Rokni M, Jensen JO, Sloth M, Filinchuk Y, Jørgensen JE, Besenbacher F, Jensen TR. Complex hydrides for hydrogen storage – new perspectives. *Mater Today*. 2014;17:122-128.
- 2 Kim KC. A review on design strategies for metal hydrides with enhanced reaction thermodynamics for hydrogen storage applications. *Int J Energy Res*. 2018;42:1455-1468.
- 3 Chong M, Karkamkar A, Autrey T, Orimo S, Jalisatgi S, Jensen CM. Reversible dehydrogenation of magnesium borohydride to magnesium triborane in the solid state under moderate conditions. *Chem Comm*. 2011;47:1330-1332.
- 4 Chong M, Autrey T, Jensen CM. Lewis base complexes of magnesium borohydride: Enhanced kinetics and product selectivity upon hydrogen release. *Inorganics*. 2017;5:89.
- 5 Xiong Z, Chen X, Lei H, An X, Wang X, Feng S, Wang Y, Peng L, Wu W. Low temperature and hydrogen atmosphere synthesis of crystalline LiBH_4 and amorphous $\text{Li}_2\text{B}_{12}\text{H}_{12}$ mixture for hydrogen storage. *Int J Energy Res*. 2014;38:254-258.
- 6 Chen P, Xiong Z, Luo J, Lin J, Tan KL. Interaction between lithium amide and lithium hydride. *J Phys Chem B*. 2003;107:10967-10970.
- 7 Hao T, Matsuo M, Nakamori Y, Orimo S. Impregnation method for the synthesis of Li-N-H systems. *J Alloys Compd*. 2008;458:L1-L5.
- 8 Chen P, Xiong Z, Yang L, Wu G, Luo W. Mechanistic investigations on the heterogeneous solid-state reaction of magnesium amides and lithium hydrides. *J Phys Chem B*. 2006;110:14221-14225.
- 9 Brack B, Dann SE, Wijayantha KGU, Adcock P, Foster S. An assessment of the viability of hydrogen generation from the reaction of silicon powder and sodium hydroxide solution for portable applications. *Int J Energy Res*. 2017;41:220-228.
- 10 Leardini F, Ares JR, Bodega J, Fernández JF, Ferrer IJ, Sánchez C. Reaction pathways for hydrogen desorption from magnesium hydride/hydroxide composites: bulk and interface effects. *Phys Chem Chem Phys*. 2010;12:572-577.
- 11 Yu P, Chua YS, Cao H, Xiong Z, Wu G, Chen P. Hydrogen storage over alkali metal hydride and alkali metal hydroxide composites. *J Energy Chem*. 2014;23:414-419.
- 12 Mao J, Gu Q, Gregory DH. Revisiting the hydrogen storage behaviour of the Na-O-H system. *Materials*. 2015;8:2191-2203.
- 13 Xu Q, Wang R, Kiyobayashi T, Kuriyama N, Kobayashi T. Reaction of hydrogen with sodium oxide: A reversible hydrogenation/dehydrogenation system. *J Power Sources*. 2006;155:167-171.
- 14 Thermodynamic database *MALT 2*. Kagaku Gijutsu-Sha; 1992.
- 15 Wang J, Liu T, Wu G, Li W, Liu Y, Araújo CM, Scheicher RH, Blomqvist A, Ahuja R, Xiong Z, Yang P, Gao M, Pan H, Chen P. Potassium-modified $\text{Mg}(\text{NH}_2)_2/2\text{LiH}$ system for hydrogen storage. *Angew Chem Int Ed*. 2009;48:5828-5832.
- 16 Wang J, Chen P, Pan H, Xiong Z, Gao M, Wu G, Liang C, Li C, Li B, Wang J. Solid-solid heterogeneous catalysis: The role of potassium in promoting the dehydrogenation of the $\text{Mg}(\text{NH}_2)_2/2\text{LiH}$ composite. *ChemSusChem*. 2013;6:2181-2189.
- 17 Dong BX, Wang L, Ge J, Ping C, Teng YL, Li ZW. The effect of KH on enhancing the dehydrogenation properties of the Li-N-H system and its catalytic mechanism. *Phys Chem Chem Phys*. 2018;20:11116-11122.
- 18 Lin HJ, Li HW, Paik B, Wang J, Akiba E. Improvement of hydrogen storage property of three-component $\text{Mg}(\text{NH}_2)_2\text{-LiNH}_2\text{-LiH}$ composites by additives. *Dalton Trans*. 2016;45:15374-15381.

-
- 19 Wang G, Carr CL, Zhao D, Sorte EG, Ellis-Caleo T, Conradi MS, Bowman Jr. RC, Majzoub EH. Density functional theory of MH-MOH solid solubility (M = Alkali) and experiments in NaH-NaOH. *J Phys Chem C*. 2015;119:8062–8069.
- 20 Kawakami M, Kuriwa T, Kamegawa A, Takamura H, Okada M, Kaburagi T. Optimum hydrogen desorption properties in LiH-LiOH composites. *Materials Transactions*. 2009;50:1855-1858.
- 21 Vajo JJ, Skeith SL, Mertens F, Jorgensen SW. Hydrogen-generating solid-state hydride/hydroxide reactions. *J Alloys Compd*. 2005; 390:55-61.
- 22 Douglas TB, Dever JL. Anhydrous sodium hydroxide: The heat content from 0° to 700 °C, the transition temperature, and the melting point. *Journal of Research of the National Bureau of Standards*. 1954;53:81-90.
- 23 Hanlon JM. Synthesis and characterisation of direct and indirect hydrogen storage materials. *Ph.D thesis*. University of Glasgow; 2013.
- 24 Sorte EG, Majzoub EH, Ellis-Caleo T, Hammann BA, Wang G, Zhao D, Bowman Jr. RC, Conradi MS. Effects of NaOH in solid NaH: Solution/Segregation phase transition and diffusion acceleration. *J Phys Chem C*. 2013;117:23575-23581.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

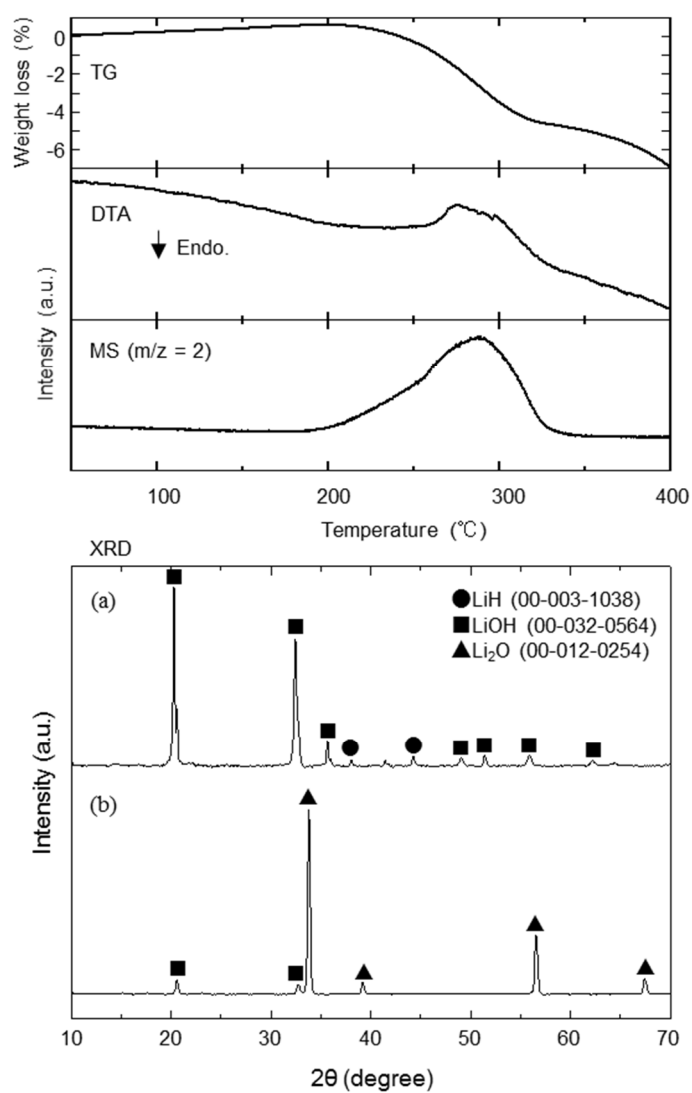


FIGURE 1 TG-DTA-MS and XRD profiles of LiH + LiOH with 1 : 1 molar ratio, (a) after milling and (b) after heating to 400 °C.

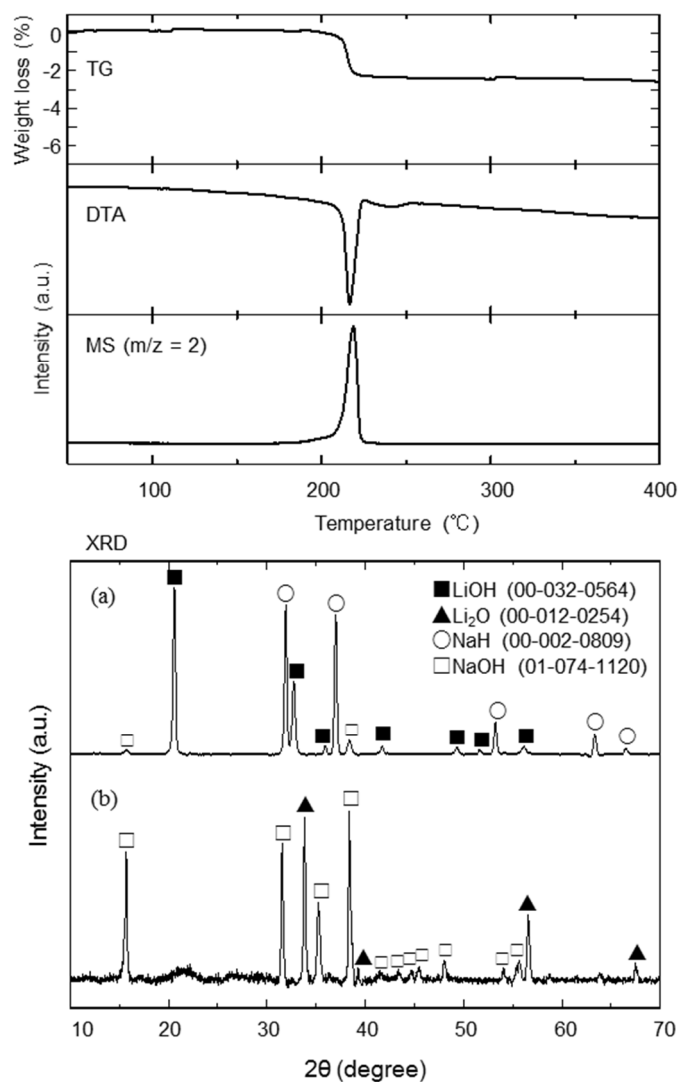


FIGURE 2 TG-DTA-MS and XRD profiles of NaH + LiOH with 1 : 2 molar ratio, (a): after milling and (b) after heating to 400 $^{\circ}\text{C}$.

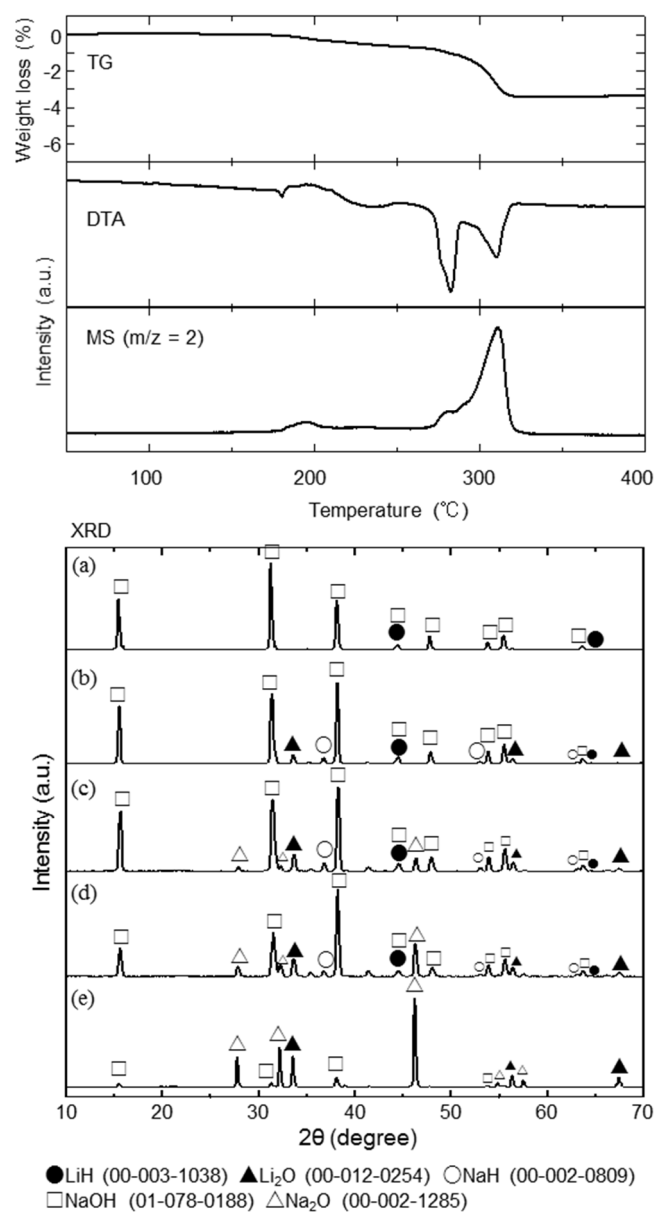


FIGURE 3 TG-DTA-MS and XRD profiles of LiH + NaOH with 1 : 1 molar ratio, (a): after milling, (b): after heating to 208 °C, (c): after heating to 262 °C, (d): after heating to 287 °C and (e) after heating to 400 °C.

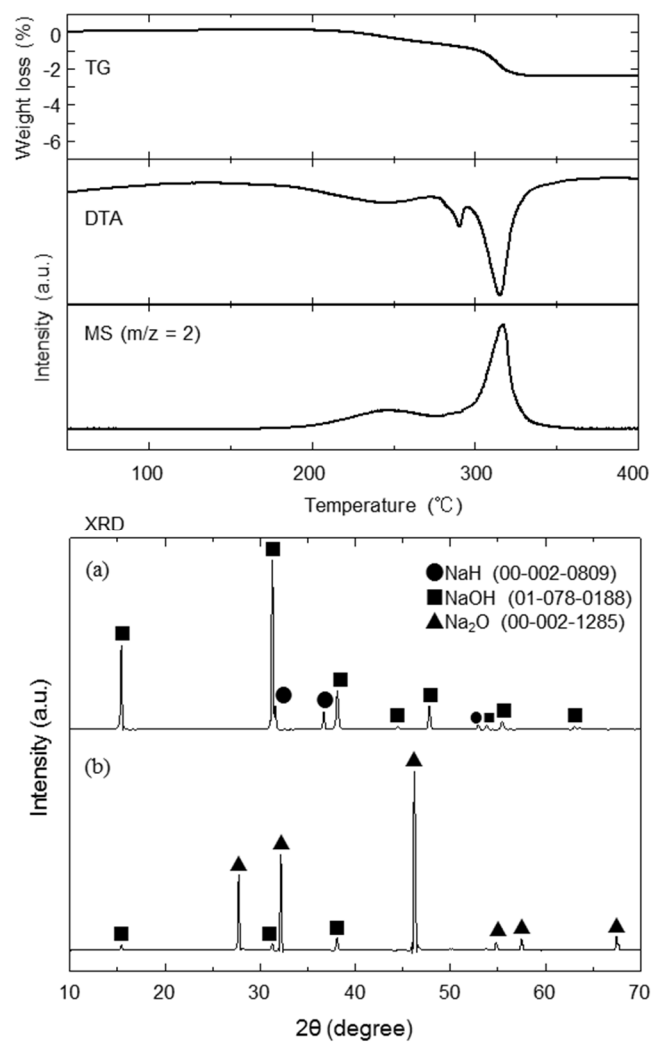


FIGURE 4 TG-DTA-MS and XRD profiles of NaH + NaOH with 1 : 1 molar ratio, (a): after milling and (b) after heating to 400 °C.

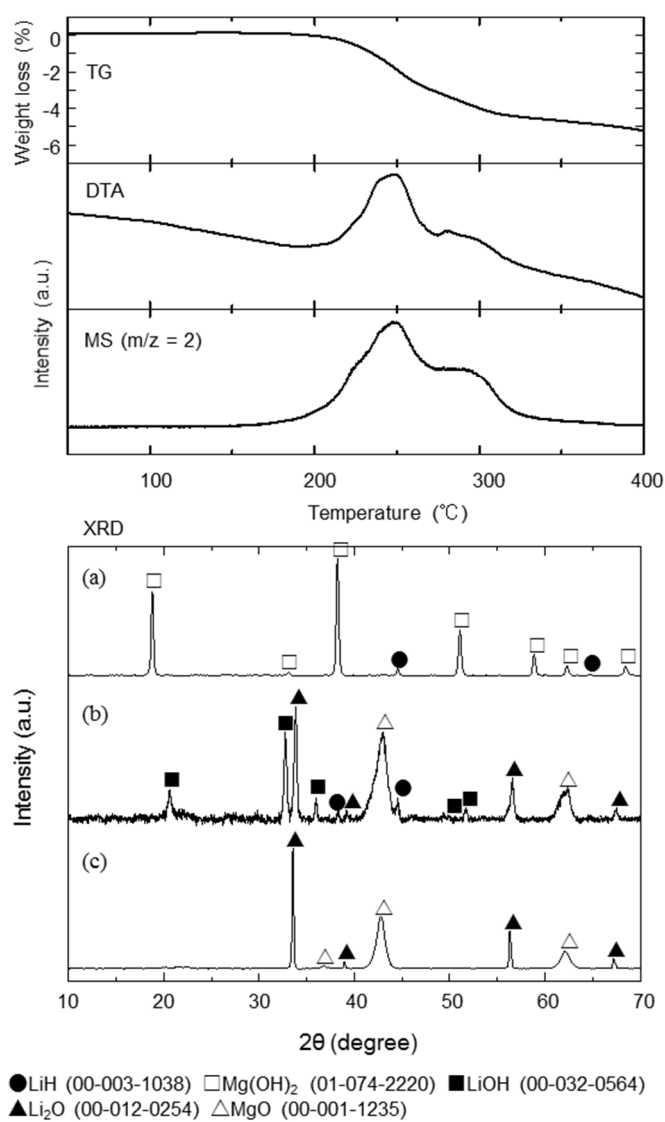


FIGURE 5 TG-DTA-MS and XRD profiles of LiH + Mg(OH)₂ with 2 : 1 molar ratio, (a): after milling, (b): after heating to 270 °C and (c): after heating to 400 °C.

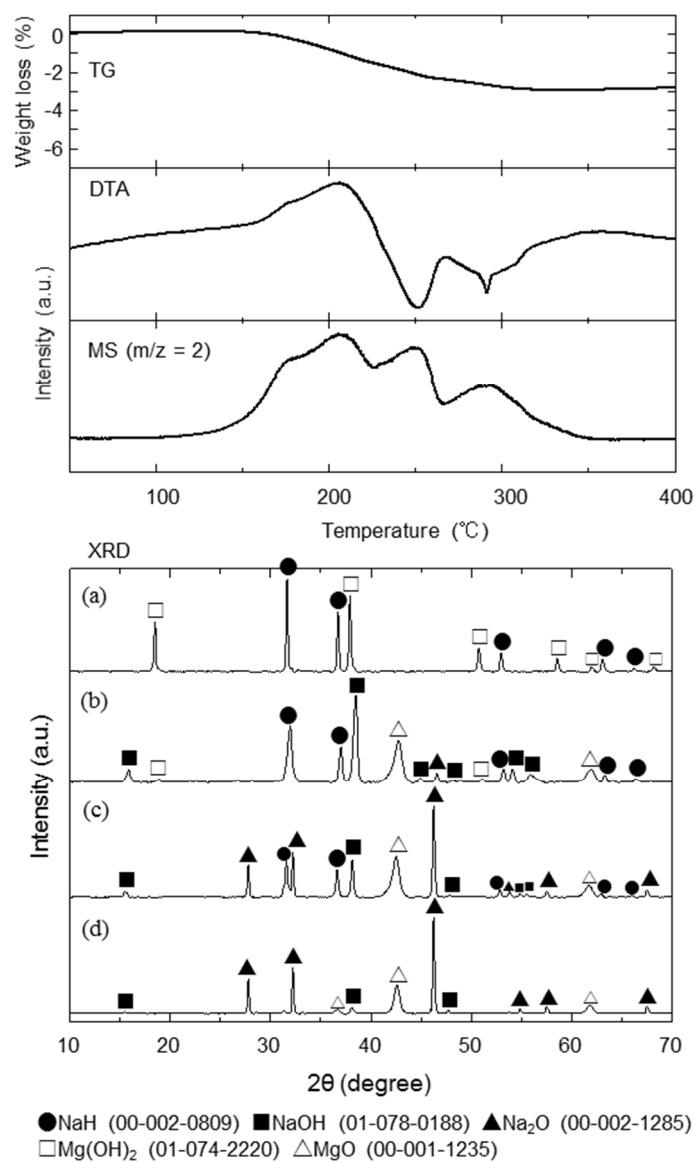


FIGURE 6 TG-DTA-MS and XRD profiles of NaH + Mg(OH)₂ with 2 : 1 molar ratio, (a): after milling, (b): after heating to 228 °C, (c): after heating to 270 °C and (d): after heating to 400 °C.

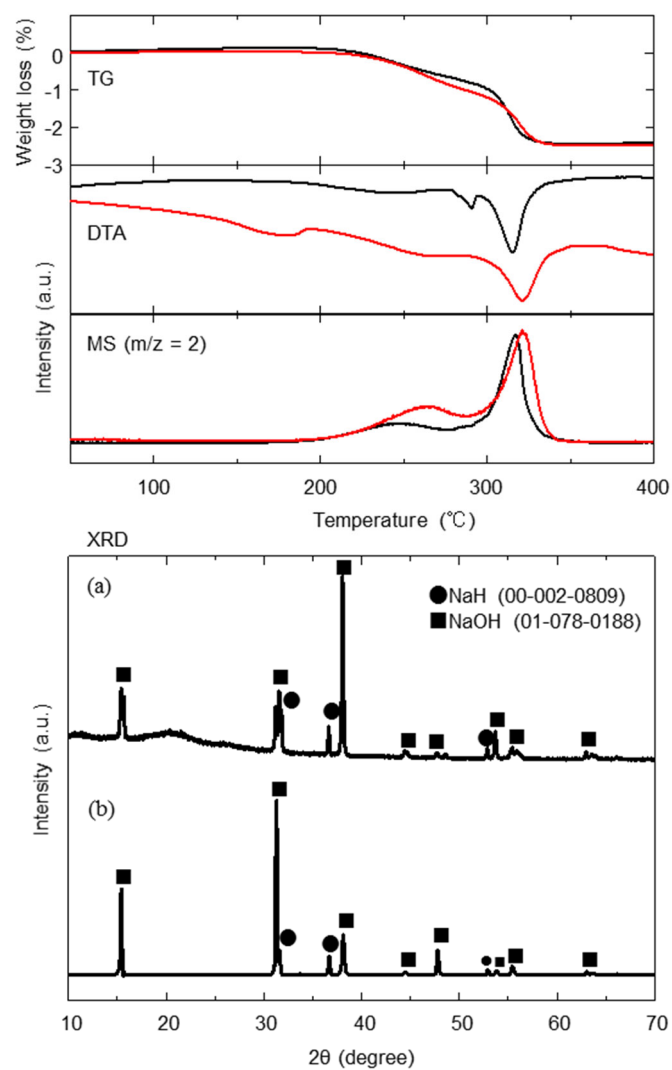


FIGURE 7 TG-DTA-MS profiles of NaH + NaOH (black lines, reference from FIGURE 4) and NaH + NaOH after rehydrogenation (red lines), and XRD profiles of NaH + NaOH, (a): after rehydrogenation and (b): after milling (reference from FIGURE 4).

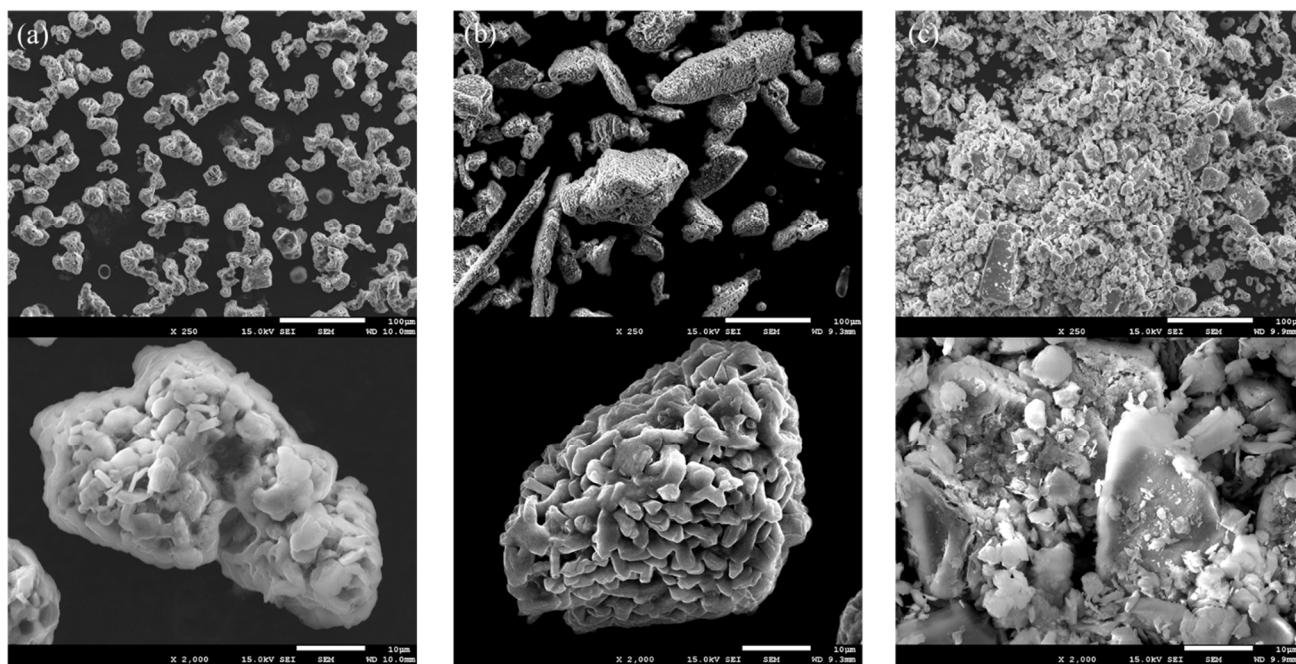


FIGURE 8 SEM images of (a) pristine NaH, (b) pristine NaOH and (c) NaH + NaOH after milling. The figures on the top were observed with a low magnification of $\times 250$ and those on the bottom were observed with a high magnification of $\times 2000$.

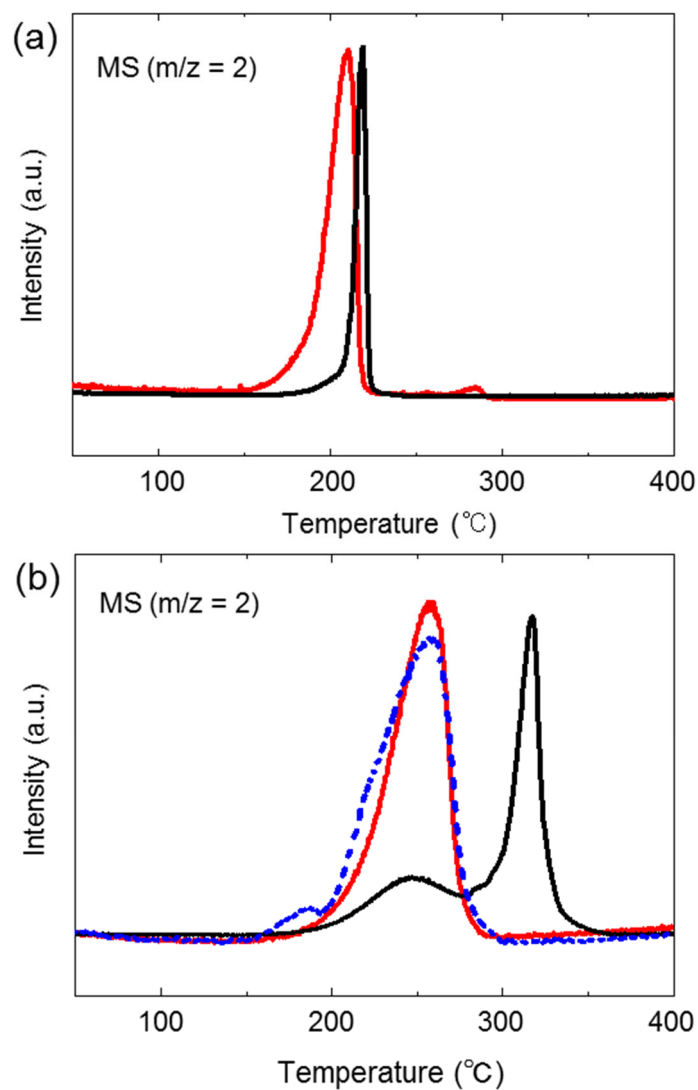


FIGURE 9 MS profiles of KH-added (a) NaH + LiOH and (b) NaH + NaOH. The red line shows the profile of 1 mol% KH added composite. The black line shows the profile without KH (reference from FIGURE 2 and FIGURE 4). The blue dashed line in FIGURE 9(b) shows the profile of KH-added composite after rehydrogenation.

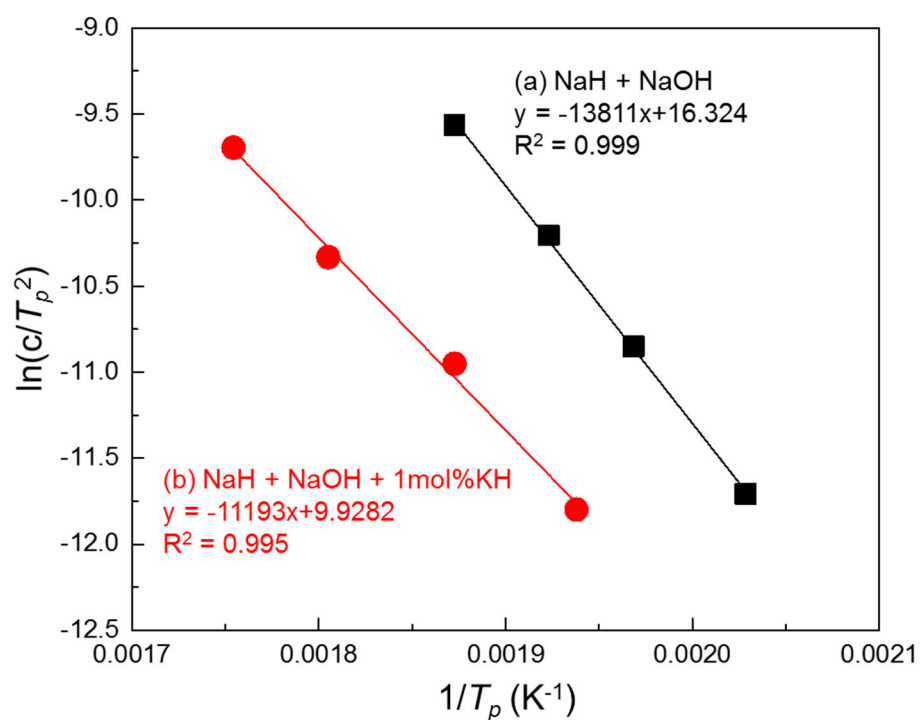


FIGURE 10 Kissinger plots for (a) NaH + NaOH and (b) 1 mol% KH added NaH + NaOH. The heating rates were 2, 5, 10 and 20 °C min⁻¹.