

Short communication

## Reaction of hydrogen with sodium oxide: A reversible hydrogenation/dehydrogenation system

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### Abstract

Sodium oxide, Na<sub>2</sub>O, reversibly absorbs hydrogen, H<sub>2</sub>, to form sodium hydride, NaH, and sodium hydroxide, NaOH, which possesses a potential to find its application to reversible hydrogen storage. X-ray diffraction measurements illustrate reversible phase and composition changes during the hydrogen absorption and desorption in the Na–O–H system. Pressure–composition (P–C) isotherm and thermogravimetric (TG) measurements exhibit a hydrogen capacity up to 3.0 wt.%. Temperature-programmed desorption (TPD) measurements demonstrate that mixing NaOH to NaH significantly shifts the hydrogen desorption of NaH towards lower temperature, to which TiCl<sub>3</sub> and SiO<sub>2</sub> show catalytic activity. A reaction intermediate, Na–H<sup>δ-</sup> ··· H<sup>δ+</sup>–ONa, involving dihydrogen bonding between the negatively charged hydrogen atom bonded to sodium and the positively charged hydrogen atom bonded to oxygen is proposed for the reaction mechanism.

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### 1. Introduction

Global energy consumption is expected to increase dramatically in the next decades. Among the various alternative energy strategies, constructing an energy infrastructure that uses hydrogen, the third most abundant element on the earth's surface, as the primary carrier connecting a host of energy source to diverse end uses, such as hydrogen-fuel cell vehicles and portable electronics, may enable a secure and clean energy future. Effective storage and delivery of hydrogen – produced from diverse sources and intended for diverse uses – are key elements of the hydrogen economy [1].

Besides the storage of hydrogen as a compressed gas or as a cryogenic liquid, solid-state storage refers to the storage of hydrogen in metal hydrides, nanostructured materials, and chemical storage materials [1]. Over the past four decades, materials for solid-state hydrogen storage have been nearly exclusively metals and metallic alloys but none of these materials has yet been demonstrated to meet the transportation

requirements. The major problems include cost, low specific uptake by weight, unfavorable kinetics requiring heating cycles, and susceptibility to contamination. The nanostructured materials, such as various carbon-based adsorbents, have also been studied for hydrogen storage and, while promising, have been beset by mixed results. Chemical storage materials such as alanates (aluminumhydrides), in which the Al atom is surrounded by four to six hydrogen atoms forming a complex negatively charged anion [2–4], and lithium imides [5] provide high contents of hydrogen on a mass basis whereas it is required for practical use to lower the high temperatures and to improve the limited kinetics for absorbing/desorbing hydrogen. From the above points of view, finding effective hydrogen storage materials is one of the most difficult challenges facing hydrogen-powered transportation and its solution requires breakthroughs in material performance coming from wide-range innovative basic researches that look beyond the storage materials currently known.

Here we report a different material system, sodium oxide, which shows a potential as a hydrogen storage medium. Sodium oxide, Na<sub>2</sub>O, has been well studied since last century and widely used in pharmaceuticals, ceramics, and chemistry

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[6–8]. Using a variety of techniques, we demonstrate that this compound can reversibly take up 3.0 wt.% hydrogen to form sodium hydride, NaH, and sodium hydroxide, NaOH. The present Na–O–H system extends hydrogen storage materials, which have been limited thus far in elements before group 15, to group-16-elements. Despite the high temperature and low equilibrium pressure for hydrogen release under the present condition, we suggest that more investigation might make the safe, contamination-free and easy-to-handle Na–O–H system a possible route to reversible hydrogen storage.

## 2. Experimental

Sodium oxide (97%, Aldrich) was used without further purification. Sodium hydroxide (>99%, Kanto Chemical) was degassed at 90 °C under high vacuum for 6 h. Sodium hydride (60% in oil, Kishida Chemical) was washed with *n*-pentane and then dried at 60 °C under high vacuum for 6 h. All the materials were stored in a dry-box under an argon atmosphere. The samples were prepared by ball-milling using a Fritsch P-6 mixer with a frequency of 300 cycles per minute for 150 min, during which a 10 min interval was held between every two 10 min ball-milling processes to suppress the temperature increase. Usually, sodium oxide was ball-milled under 0.4 MPa Ar, while the NaH/NaOH samples were milled under 0.4 MPa H<sub>2</sub>.

A Rigaku RINT-2000 X-ray diffractometer with Cu K $\alpha$  radiation (40 kV, 150 mA) was used to identify structural/compositional changes. The samples at different degrees of hydrogenation were obtained after various stages of reaction with H<sub>2</sub> and the samples at different degrees of dehydrogenation were obtained at various stages of degassing at 270 °C under dynamic vacuum using a rotary pump. A glass substrate holding the powder sample was covered by an adhesive tape on the surface to prevent the sample from reaction with oxygen and moisture during the measurements.

Hydrogen uptake by Na–O–H system was measured with a Sieverts' type apparatus (P69-17, Suzuki Shokan Co. Ltd.). Static pressure–composition isotherms (PCI) were determined at temperatures of 150, 175, 200, 225 and 250 °C. The delay time was extended to 300 s; that is, data were recorded only when there was no pressure change within 300 s. The dimensions of the sample cell are about 2.8 cm<sup>3</sup> in volume. A sample of approximately 300 mg was tested each time. A tube furnace with accuracy of 0.1 °C was used as a heater. A thermocouple was closely contacted to the outer surface of the hydrogenation chamber. Kinetics of hydrogen absorption was also measured using the same apparatus. The sample was heated to desired temperatures, and then, the sample chamber was flushed with hydrogen of desired pressure. Hydrogen absorption was measured with time.

Weight variation of dehydrogenation process was monitored with a Shimadzu thermogravimetric apparatus (DTG-50) with purified He as a carrier gas (150 ml min<sup>-1</sup>). The sample (typically 10 mg) was preequilibrated for 10 min

at 25 °C and then the temperature was linearly raised to 450 °C with a ramp of 2 °C min<sup>-1</sup>. Temperature-programmed desorption (TPD) measurements were conducted on a Reactor-MS system (TPD-43, BEL Japan Inc.) with purified He as a carrier gas (150 ml min<sup>-1</sup>). Around 125 mg of sample was tested each time. The outlet gas was detected by Mass-Spectrometer during the desorption of samples with raising the temperature at 2 °C min<sup>-1</sup> from 25 to 450 °C.

## 3. Results and discussion

We performed X-ray diffraction measurements on sodium oxide, and its partly hydrogenated, fully hydrogenated, partly dehydrogenated and fully dehydrogenated samples for investigating the phase and composition changes during hydrogen absorption and desorption in the Na–O–H system. The results (Fig. 1) show that the cubic Na<sub>2</sub>O phase transforms to cubic sodium hydride and orthorhombic sodium hydroxide phases [9–11] after being hydrogenated and the phase changes in desorption follow a process almost the reverse of that of absorption. For the fresh Na<sub>2</sub>O sample prepared by ball-milling under an Ar atmosphere (Fig. 1a), diffractions from the cubic Na<sub>2</sub>O phase were observed along with very weak peaks due to small amounts of impurities Na<sub>2</sub>O<sub>2</sub> and NaOH. It was found that the diffraction pattern remained unchanged after exposure of Na<sub>2</sub>O to 20 MPa H<sub>2</sub> at room temperature for 48 h. Upon exposing the Na<sub>2</sub>O sample to 10 MPa H<sub>2</sub> at a temperature as low as 60 °C for 48 h, diffractions due to cubic sodium hydride and orthorhombic sodium hydroxide phases were observed at the expense of the sodium oxide diffractions with a nearly 50% conversion (Fig. 1b). The impurity Na<sub>2</sub>O<sub>2</sub> disappeared during the reaction and did not recover thereafter. By raising the temperature to 150 °C, the reaction of fresh Na<sub>2</sub>O with 10 MPa H<sub>2</sub> for 48 h resulted in

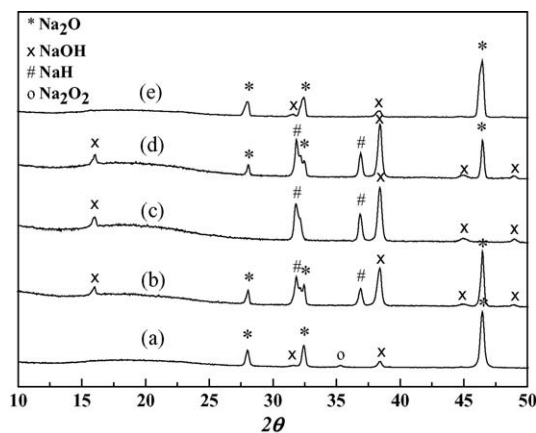


Fig. 1. Structure changes during hydrogenation and dehydrogenation processes. (a) Na<sub>2</sub>O; (b) partly hydrogenated sample; (c) fully hydrogenated sample; (d) partly dehydrogenated sample; (e) fully dehydrogenated sample. Peaks marked with an asterisk are characteristic diffraction of Na<sub>2</sub>O, crosses of NaOH, hashes of NaH and circles of impurity Na<sub>2</sub>O<sub>2</sub>. Sample collection and details for measurements are described in the text.

a full conversion to NaH and NaOH (Fig. 1c). By evacuating the hydrogenated sample at 270 °C for 30 min using a rotary pump, the diffractions due to the cubic Na<sub>2</sub>O phase recovered at the expense of the NaOH and NaOH diffractions with a nearly 50% conversion (Fig. 1d) and a continued evacuation at the same temperature for 3 h led to a complete recovery of Na<sub>2</sub>O (Fig. 1e). Similar results were observed for samples prepared by repeating the hydrogenation and dehydrogenation processes for three times. We also noted that ball-milling Na<sub>2</sub>O under a 0.4 MPa H<sub>2</sub> atmosphere (instead of Ar) directly led to a complete conversion to NaH and NaOH. Therefore, the reactions observed above can be formulated as shown in Eq. (1). In this reaction, the molar ratio of absorbed H<sub>2</sub> molecules to Na<sub>2</sub>O molecules is one, corresponding to a theoretical hydrogen capacity of 3.1 wt.%.



Pressure–composition (P–C) isotherms of fresh Na<sub>2</sub>O samples were measured at several temperatures to quantitatively characterize the hydrogenation property of Na<sub>2</sub>O, which exhibit that about 3.0 wt.% hydrogen can be absorbed by Na<sub>2</sub>O (Fig. 2), in agreement with the stoichiometry in Eq. (1). The absorption isotherms at 175, 200, 225 and 250 °C are close to each other, exhibiting hydrogen absorptions up to 3.0 wt.% at 1.8 MPa, whereas the one at 150 °C shows slightly less hydrogen absorption (ca. 2.85 wt.% at 1.8 MPa). Na<sub>2</sub>O has fast kinetics in hydrogen absorption. Fig. 3 shows that at a pressure of 0.12 MPa, 1.5 wt.% hydrogen can be absorbed in 20 min at 150 °C and more than 2.0 wt.% hydrogen can be absorbed in 5 min at 175–250 °C.

In the PCI measurements, the equilibrium pressure at each temperature was rather low (below 0.005 MPa), suggesting that the absorbed hydrogen might not be easily desorbed. Actually the desorption stopped at low pressures (below 0.005 MPa), which consequently obstructed the measurements of desorption isotherms under the present apparatus condition. For desorbing hydrogen from the hydrogenated samples, dynamic evacuation was continued at 270 °C for

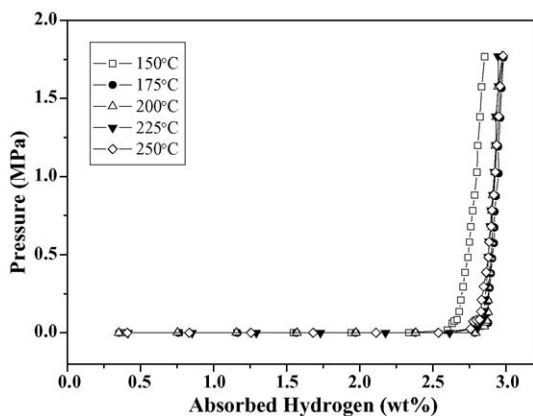


Fig. 2. Pressure–composition (P–C) isotherms of Na<sub>2</sub>O at various temperatures. Pressure was increased step by step to 1.8 MPa and the other details are given in the text.

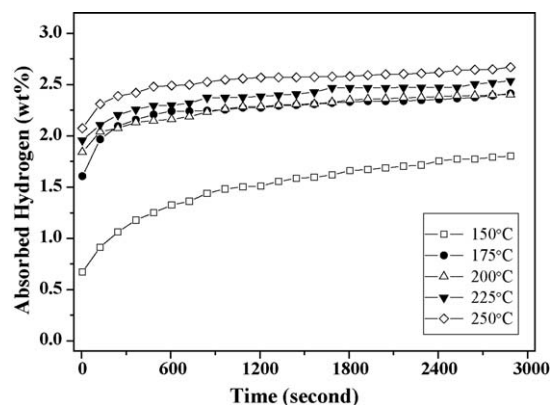


Fig. 3. Kinetics of hydrogen absorption of Na<sub>2</sub>O at various temperatures.

3 h using a rotary pump. No significant differences in the absorption isotherms were observed for the second and third cycles.

Thermogravimetric (TG) measurements were carried out to investigate the desorption process of the Na–O–H system. As the desorption isotherms could not be recorded under the present apparatus condition, the TG measurements provide important quantitative information. Fig. 4 shows that within the examined temperature range, hydrogen desorbs from the ball-milled NaH and the ball-milled NaH/NaOH (1:1) mixture with rather different behavior. In the case of NaH, the desorption started at ca. 300 °C and ended at ca. 370 °C with a weight loss was 3.9 wt.% (Fig. 4a), close to the theoretical value of 4.1 wt.%. In the case of NaH/NaOH (1:1), the desorption started at ca. 160 °C and ended at ca. 310 °C with a weight loss of 3.0 wt.% (Fig. 4b), in agreement with the stoichiometry of Eq. (1). By mixing with equimolar NaOH the hydrogen desorption shifts by about 100 °C toward lower temperatures.

Temperature-programmed desorption (TPD) experiments were also performed to investigate the dehydrogenation process of the Na–O–H system. The released gas was identified by TPD–Mass spectrometry. Only hydrogen was found to be released in the tested temperature range with an exception

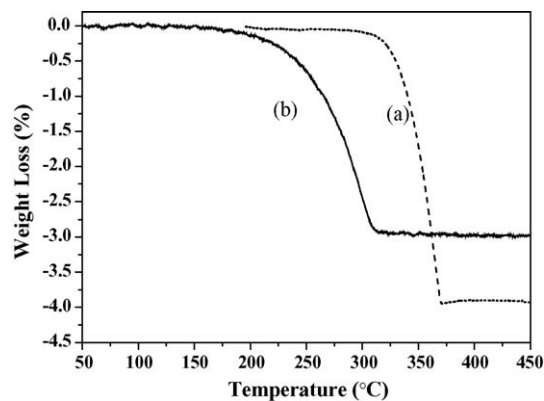


Fig. 4. Weight loss during hydrogen desorption process over (a) the ball-milled NaH and (b) the ball-milled NaH/NaOH (1:1) mixture.

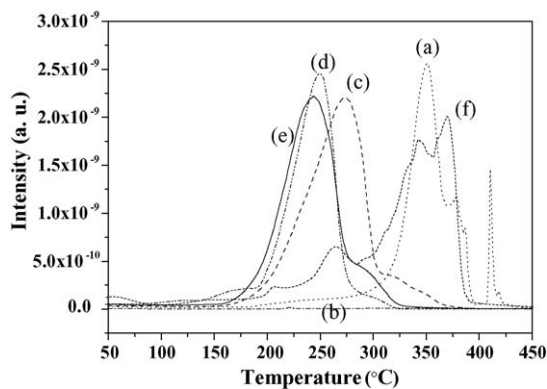


Fig. 5. Temperature-programmed desorption of Na–O–H Sample. H<sub>2</sub> signal was detected by Mass-Spectrometer in the desorption of (a) NaH, (b) NaOH, (c) Na/NaOH(1:1), (d) NaH/NaOH (1:1) doped with 1 mol% TiCl<sub>3</sub>, (e) NaH/NaOH (1:1) doped with 5 mol% SiO<sub>2</sub>, and (f) hydrogenated Na<sub>2</sub>O sample annealed under an H<sub>2</sub> atmosphere to 360 °C. Samples (a)–(e) were prepared by ball-milling under an atmosphere of 0.4 MPa H<sub>2</sub>. H<sub>2</sub> signals were detected by Mass-Spectrometer in the H<sub>2</sub> desorption of the samples with raising the temperature at 2 °C min<sup>-1</sup> from 25 to 450 °C.

for a small amount of H<sub>2</sub>O which appeared at the expense of the background O<sub>2</sub> at the same temperature as that for the H<sub>2</sub> desorption. We have also observed the same for the hydrogen desorption of various metal hydrides (M–H) and we assign the H<sub>2</sub>O peak to the product of reaction of H<sub>2</sub> with O<sub>2</sub> in the mass spectrometry system. Fig. 5 shows the H<sub>2</sub> signals in the desorption of (a) NaH, (b) NaOH, (c) Na/NaOH(1:1), (d) NaH/NaOH (1:1) doped with 1 mol% TiCl<sub>3</sub> and (e) NaH/NaOH (1:1) doped with 5 mol% SiO<sub>2</sub>. Each sample was prepared by ball-milling under an atmosphere of 0.4 MPa H<sub>2</sub>. A large H<sub>2</sub> desorption peak was observed for NaH at 352 °C (Fig. 5a), whereas no H<sub>2</sub> desorption was observed for NaOH (Fig. 5b). Mixing NaOH to NaH with a 1:1 molar ratio resulted in a shift of desorption temperature to 273 °C (Fig. 5c), in agreement with the TG measurements. For alanates as hydrogen storage materials, it was reported that upon doping with selected titanium compounds, the dehydrogenating could be kinetically enhanced under moderate conditions in the solid state and this has been followed by further progress in the development of a variety of catalysts for the reversible dehydrogenating of NaAlH<sub>4</sub> [2–4]. We found that TiCl<sub>3</sub> also acted as an active catalyst for the dehydrogenation of the Na–O–H system (Fig. 5d). In addition, it was found that SiO<sub>2</sub>, an excellent catalyst used for the dehydrogenation of LiBH<sub>4</sub> [12], was more catalytically active than TiCl<sub>3</sub> for this reaction (Fig. 5e). Interestingly, annealing the hydrogenated sample under an H<sub>2</sub> atmosphere at 360 °C led to a significant increase in the H<sub>2</sub> desorption temperature (Fig. 5f).

The reaction, Na<sub>2</sub>O + H<sub>2</sub> ↔ NaH + NaOH (1), has a reaction heat of –15.38 kcal mol<sup>-1</sup>, in comparison with the value of –26.95 kcal mol<sup>-1</sup> for the reaction, 2Na + H<sub>2</sub> ↔ 2NaH [13–15]. In the present work, we found that the mixing of NaOH to NaH results in a significant decrease in the hydrogen desorption temperature of NaH. It is reasonable to consider

that a reaction intermediate, Na–H<sup>δ-</sup>...H<sup>δ+</sup>–ONa, involving dihydrogen bonding [16–19] between the negatively charged hydrogen atom bonded to sodium and the positively charged hydrogen atom bonded to oxygen might play an important role in both the hydrogenation and dehydrogenation processes of the Na–O–H system.

We have noted that there have been a number of studies dealing with the ternary system Na–NaOH–Na<sub>2</sub>O–NaH since the rapid detection of sodium–water leaks in the secondary heat exchangers of liquid metal fast breeder reactors (LMFBR) is of critical importance [20,21]. Solutions of hydrides in alkali metal hydroxides are also of value for industrial removal of oxides from the surface of metal articles and phase diagrams of the NaH and NaOH system have been reported [22]. A striking feature in the previous report is that the dissolution of the hydride in the hydroxide appreciably increased its thermal stability and extended the temperature at which sodium hydride can be used above 500 °C [22]. Even for compositions with >40% NaH, corresponding to the heterogeneous region in the phase diagram, the dissociation of the excess of hydride proceeded at temperatures higher than that of pure NaH. We noted that the samples in the previous report were prepared at temperatures above the melting points and the increase of the dissociation temperature for NaH over that of pure NaH was explained by the ability of the molten NaOH to envelop the hydride to prevent it from H<sub>2</sub> release [22]. Indeed, the same was observed in the present work. The hydrogenated Na<sub>2</sub>O sample annealed to 360 °C under an H<sub>2</sub> atmosphere showed much higher thermal stability (Fig. 5f). In contrast, it seems that hydrogen can be smoothly released when the reaction takes place at the interface of NaH and NaOH particles. For facilitating the hydrogen release from the Na–O–H, it is important to keep the samples below the melting point of NaOH to prevent them from the formation of solid solution and from the envelopment of NaH into NaOH.

#### 4. Conclusions

There have been thus far a large number of hydrogen storage materials with elements in groups 1–15. In the present work, we have found that the Na–O–H system can reversibly absorb/desorb hydrogen up to 3.0 wt.%, extending reversible hydrogen storage materials to group 16 elements. Further works are needed for better understanding of the reaction mechanism and for improving the performance of the safe, contamination-free and easy-to-handle system to meet practical applications.

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