

Hydrogen storage over alkali metal hydride and alkali metal hydroxide composites

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Abstract

Alkali metal hydroxide and hydride composite systems contain both protic (H bonded with O) and hydridic hydrogen. The interaction of these two types of hydrides produces hydrogen. The enthalpy of dehydrogenation increased with the increase of atomic number of alkali metals, i.e., -23 kJ/mol_{H₂} for LiOH-LiH, 55.34 kJ/mol_{H₂} for NaOH-NaH and 222 kJ/mol_{H₂} for KOH-KH. These thermodynamic calculation results were consistent with our experimental results. H₂ was released from LiOH-LiH system during ball milling. The dehydrogenation temperature of NaOH-NaH system was about 150 °C; whereas KOH and KH did not interact with each other during the heating process. Instead, KH decomposed by itself. In these three systems, NaOH-NaH was the only reversible hydrogen storage system, the enthalpy of dehydrogenation was about 55.65 kJ/mol_{H₂}, and the corresponding entropy was ca. 101.23 J/(mol_{H₂}·K), so the temperature for releasing 1.0 bar H₂ was as high as 518 °C, showing unfavorable thermodynamic properties. The activation energy for hydrogen desorption of NaOH-NaH was found to be 57.87 kJ/mol, showing good kinetic properties.

Key words

hydrogen storage; alkali metal hydroxide; alkali metal hydride; thermodynamic; kinetic

1. Introduction

Tremendous efforts have been devoted to the development of light-weight, high hydrogen content chemicals for on-board hydrogen storage application in the past two decades. Among all the materials investigated, borohydrides, analates [1,2], ammonia borane and derivatives [3–5] and amide-hydride composites [6–8] possess higher hydrogen storage capacity. In particular, the amide-hydride system possesses a distinct feature among others, i.e., there are oppositely charged hydrogen atoms in the system, in which hydrogen atom attached to nitrogen bears positive charge and hydrogen bonded with metal is negatively charged. The chemical potential for the combination of two oppositely charged atoms is likely to be the driving force for the hydrogen desorption from the amide-hydride composites [6]. Similarly, metal hydroxide and hydride composite also possess protic (H bonded with O) and hydridic hydrogen. It is, therefore, of our interest to figure out the interaction of hydroxide and hydride. As

we known, Vajo et al. [9] investigated hydrogen desorption on LiOH-LiH system, and they found that the reaction occurs upon heating with H₂ evolution beginning at ~ 50 °C and completes at 200 – 300 °C. They said that ball milling only plays a role as the physically mixed of LiH and LiOH. To the best of our knowledge, Xu et al. [10] investigated hydrogen absorption on Na₂O and found that ca. 3.0 wt% hydrogen could be reversibly stored through the reaction of $\text{Na}_2\text{O} + \text{H}_2 \rightleftharpoons \text{NaOH} + \text{NaH}$. But they didn't give the thermodynamic data because of the detection limit of their instrument, neither study the kinetic properties of NaOH-NaH system. So far, no literature report has been found on the hydrogen storage properties of KOH-KH system. In this work, three hydroxide-hydride systems, i.e., LiOH-LiH, NaOH-NaH and KOH-KH, were investigated.

Our experimental results showed that ca. 0.96 equiv. H₂ was released from LiOH-LiH system during ball milling (enthalpy changes of LiOH-LiH reaction was calculated to be -23 kJ/mol_{H₂}). Thermodynamic and kinetic analyses revealed that although NaOH-NaH can produce H₂ starting at

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175 °C, the temperature for releasing H₂ at 1.0 bar equilibrium pressure is ~518 °C, showing unfavorable thermodynamic properties. Unlike the other two composites which form oxides as solid products, KH decomposes alone, resulting in that H₂ does not react with KOH.

2. Experimental

2.1. Samples preparation

LiOH (98%) and LiH (98%) were purchased from Alfa Aesar. KOH was purchased from Aladdin with purity of 99.999% (purity excludes sodium content). KH was purchased from Alfa Aesar with 30% w/w in mineral oil. NaH (95%) and NaOH (98%) were purchased from Sigma-Aldrich. LiOH, NaOH and KOH were firstly crashed into fine powder by a Retsch planetary mill (PM-400). NaOH and KOH were dried in vacuum at 400 °C and in Ar gas at 300 °C respectively, to remove water. KH was washed by cyclohexane to remove mineral oil. LiH and NaH were directly used without further treatment. In order to avoid air and moisture contamination, all the samples handlings were conducted in a MBRAUN glove box filled with purified argon.

LiOH-LiH, KOH-KH and NaOH-NaH were prepared by ball milling hydroxide and hydride in a molar ratio of 1 : 1 at 200 rpm on a Retsch PM400 planetary ball mill. The milling jar was equipped with gas valves which can be connected to a pressure gauge to enable the measurement of pressure increase in the jar caused by gas release during ball milling. The weight ratio of ball to sample was about 30 : 1. To inhibit powder conglutination and heat accumulation in the jar, samples were milled for 60 s in one direction, paused for 15 s and revolved to the reverse direction. The gas generated during ball milling was analyzed by mass spectrometer [11].

2.2. Methods

XRD measurements were conducted on a PANalytical X'pert diffractometer (Cu K_α, 40 kV, 40 mA). A homemade sample cell was used to protect samples from air contamination. Thermal decomposition properties of samples were analyzed on a homemade temperature-programmed desorption and mass spectrometer (MS, Hiden) combined system, which recorded the signals of H₂ (*m/z*=2) simultaneously. Pure Ar was used as the carrier gas. In each test, the sample (20 mg) was loaded and heated at a rate of 5 °C/min. The sample temperature was measured by a thermocouple that was inserted into the powder sample. About 10 mg sample was loaded in a Al₂O₃ crucible for thermogravimetric measurement on a Netzsch TG-DTA apparatus (Netzsch, Germany) with a ramping rate of 2 °C/min. An automatic gas-reaction controller from Advanced Materials Corporation was used for quantitative measurement of hydrogen absorption/desorption. The ramping rate was fixed at 0.5 °C/min in the range of 20–300 °C. Equilibrium desorption pressure measurements were carried out in an automatic Sievert-type apparatus (Hy-Energy sci-

entific instruments PCT pro-2000). ca. 0.5 g sample was loaded for testing. Kinetic properties of hydrogen desorption from NaOH-NaH system were determined by Kissinger's approach. The heating rates were 1 °C/min, 2 °C/min, 3 °C/min, 4 °C/min and 5 °C/min, respectively.

3. Results and discussion

3.1. LiOH-LiH system

The interaction between LiOH and LiH occurs upon ball milling. Figure 1 shows the plot of gas release as a function of ball milling time in which the amount of gas was calculated from the pressure increase in the milling jar by means of the state equation of ideal gas. As evidenced by the MS analysis (shown in Figure 2), hydrogen was the only detectable gaseous product from LiOH-LiH sample during the ball milling. Also shown in Figure 1, hydrogen started to evolve after milling the sample for 30 min and the rate of gas release accelerated after 3 h of ball milling. Within 7 h ca. 1.92 equiv. H (or 0.96 equiv. H₂) were detached from LiOH-LiH.

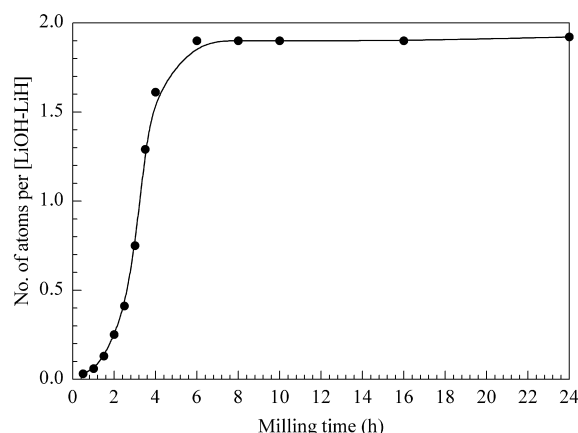


Figure 1. Time dependence of hydrogen content increase in the milling jar

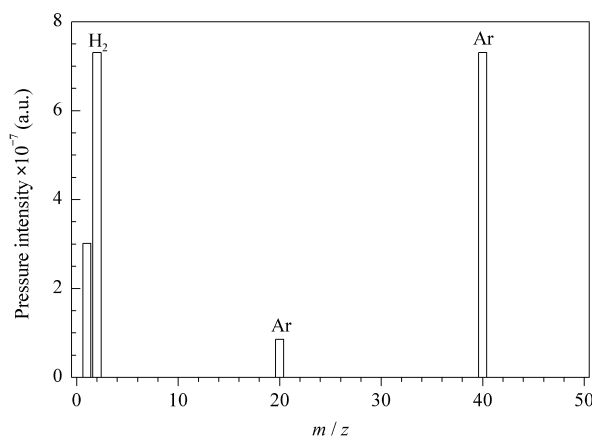


Figure 2. Mass spectrometer analysis of gases generated during ball milling

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