Journal of Alloys and Compounds 718 (2017) 134–138

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Synergic effect of $ZrCl_4$ on thermal dehydrogenation kinetics of KBH_4

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ARTICLE INFO

Article history:
Received 6 February 2017
Received in revised form
10 May 2017
Accepted 11 May 2017
Available online 12 May 2017

Keywords:
Activation energy
Catalyst
Thermal analysis
$ZrCl_4$
KBH_4

ABSTRACT

The synergic effect of zirconium tetrachloride ($ZrCl_4$) on the thermal dehydrogenation of KBH_4 has been investigated. Zirconium tetrachloride activated the KBH_4 surface during ball milling to improve the dehydrogenation kinetics. The activation energy of dehydrogenation is remarkably reduced to 162 ± 6 kJ/mol as compared to the pure KBH_4, which was found to be 274 ± 12 kJ/mol under identical experimental conditions. The reduced activation energy leads to remarkably decreased onset temperature of hydrogen desorption for catalyzed KBH_4 ($T_{onset} < 350$ °C) as compared to pure KBH_4 ($T_{onset} < 550$ °C). The reduced dehydrogenation temperature will be helpful to manage the potassium evaporation to maintain the reversibility. The Gibbs free-energy calculations and experimental results suggest that the thermal dehydrogenation proceeds via the potassium (K) intermediate rather than via potassium hydride (KH).

1. Introduction

Hydrogen storage and delivery technology based on the solid materials have been considered as one of the best options to realize the hydrogen-based energy technology [1–8]. In this regards, body-centered cubic (bcc) alloys have been sufficiently explored, however, failed to reach the desired sets target of DOE because of low hydrogen storage capacity (<2.5 wt.% H) and high materials cost [9–20]. Magnesium based materials have shown the potential to achieve the target of hydrogen storage capacity, and these are being developed for the practical applications [21–24]. Furthermore, the complex hydrides such as alanates, borohydrides, and amides have shown a large hydrogen storage capacity and, therefore, attracted attention all over the world for the stationary and mobile hydrogen storage applications [25,26]. The alkali (Li, Na, and K) and alkaline earth metals (Mg, and Ca) borohydrides, $M(BH_4)_n$ have potential to be developed as hydrogen storage materials for onboard applications [20–33]. However, the thermodynamics and kinetics of complex hydrides must be tuned for their viable commercial applications at the desired working conditions [3,25,26]. Among others, potassium borohydride (KBH_4) appears to be a promising candidate because of its hydrogen storage capacity exceeds 7.4 wt. % H [25,26]. The challenges related to KBH_4 are its high thermal dehydrogenation temperature (>550 °C, under vacuum), and its limited reversibility which required stringent temperature and pressure conditions. Therefore, limited and scattered reports are available on the thermal dehydrogenation of KBH_4 [25–28,33–38]. The thermal dehydrogenation of KBH_4 is thermodynamically feasible via the formation of potassium and boron intermediates above 710 °C under 0.1 MPa hydrogen pressure. The dehydrogenation temperature will be marginally lower under vacuum, or inert gas flow conditions. The vapor pressure of potassium will be significantly high at such a high temperature. Therefore, management of potassium evaporation is a big issue for its viable commercial application. Thus, it is desirable to lower the dehydrogenation temperature of KBH_4 to minimize the losses of potassium. Use of suitable additives could be a possible solution to reduce the dehydrogenation temperature [39–49]. Zirconium tetrachloride ($ZrCl_4$) has been found to be an appropriate catalyst for the $LiBH_4$-MgH_2 reactive composite [39] which helps to activate the surface during ball milling. The $ZrCl_4$ chemically reacts with borohydride which eventually reduced to lower chlorides ($ZrCl_3$/$ZrCl_2$) and nanosize metallic zirconium during ball milling [39]. The chemically active $ZrCl_4$ could activate the KBH_4 surface to facilitate the hydrogen release, which eventually could lower the dehydrogenation temperature. In the present study, the synergic effect of $ZrCl_4$ on dehydrogenation of KBH_4 has been investigated. The results were compared with the dehydrogenation of pure KBH_4 under similar experimental conditions. The apparent activation energy of catalyzed KBH_4 has been found to be remarkably decreased as

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http://dx.doi.org/10.1016/j.jallcom.2017.05.118
0925-8388/

compared to pure KBH_4 under the similar experimental conditions. The decreased apparent activation energy leads to a reduced dehydrogenation temperature, which could be helpful to manage the potassium evaporation to maintain the reversibility.

2. Experimental

The KBH_4 powder of purity 96.70 wt. %, and zirconium tetrachloride ($ZrCl_4$) of purity 99.99 wt. % (both were purchased from Sigma – Aldrich) were used for the preparation of catalyzed ($cKBH_4$) and pure ($pKBH_4$) samples. The $cKBH_4$ was prepared by ball milling of as received KBH_4 along with 10 wt. % $ZrCl_4$. The ball milling was carried out in 1 g batch size using a stainless steel pot contains 20 pieces of stainless steel balls of diameter 7 mm. The sample was ball milled under argon (Ar) atmosphere for 2 h in a pattern of 1-h milling and half an hour pause time. The rotation frequency was kept at 400 revolutions per minute for each batch of the samples. The $pKBH_4$ sample was prepared under the similar ball milling conditions to compare the dehydrogenation results.

The dehydrogenation experiments were conducted in a thermoanalyser (TG-DTA; TG-8120, Rigaku) unit attached with a mass spectrometer (MS; M-QA200TS, Anelva) which was kept in the inert atmosphere (argon gas) glove box. The argon gas flow rates for all the dehydrogenation experiments were 18 L/h to maintain the negligible hydrogen pressure. The phase analysis was carried out by powder-X-Ray diffractometer (XRD; RINT-2100, Rigaku, Cu-K_α radiation). Morphology and the elemental mapping were performed by a scanning electron microscopy - energy dispersive spectroscopy (SEM-EDS; JSM-6380A, JEOL).

The apparent activation energy of dehydrogenation has been evaluated by a non-isothermal process using H_2 – MS (m/z: 2) peak temperature of MS analysis. The Kissinger method (Eq. (1)) was employed to calculate the activation energy:

$$\ln\frac{\beta}{T_p^2} = -\frac{E_a}{RT_p} + ln\frac{RK_o}{E_a} \tag{1}$$

where T_p is the peak temperature of the H_2-MS analysis, β is the heating rate, E_a is the apparent activation energy, K_o is collision frequency, and R is the universal gas constant. The chemical state of the catalyst ($ZrCl_4$) in the ball milled $cKBH_4$ and after dehydrogenation was determined by X-ray photoemission spectroscopy (XPS; Thermo-Fisher Scientific, ESCALAB 250Xi, Al-K_α = 1486.6 eV) by measuring the binding energy (BE) of Zr3d electron. The sample surface was argon ion (Ar^+) sputtered before the XPS measurements to extract the real chemical state of the additive. The sample holder was appropriately grounded during XPS analysis to avoid the interference of charge accumulation over the sample surface. The sample preparation, characterization, and analysis were carried out in the argon glove box, in which oxygen and water vapor level were maintained below 2 ppm. It has been ensured that the sample should not be exposed to an open atmosphere before and during the operations.

3. Results and discussion

3.1. Thermodynamics and sample characterization

Thermodynamics of KBH_4 dehydrogenations were studied by considering the two possible reactions: (1) $KBH_4 = K + B + 2H_2$, and (2) $KBH_4 = KH + B + 1.5H_2$. The HSC *version 6.0* and *Fact-Sage* version 6.1 database were used for the calculations. The Gibbs free energy versus temperature plots is presented in Fig. 1. The most favorable dehydrogenation reaction of KBH_4 was found to be intermediated via potassium as per the reaction (2):

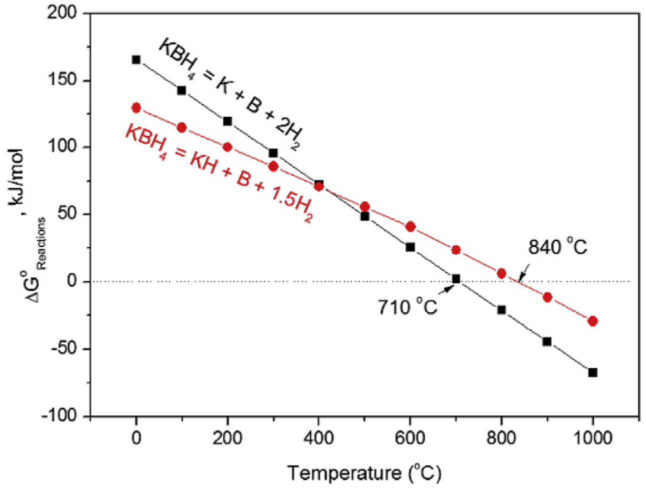

Fig. 1. The Gibbs free calculation of KBH_4 dehydrogenation with various product combinations. The dehydrogenation of KBH_4 into K, B, and H_2 is the most suitable combination as per the thermodynamics.

$$KBH_4 = K + B + 2H_2 \tag{2}$$

It is evident from Fig. 1 that the reaction (2) is feasible at the 710 °C under 0.1 MPa hydrogen pressure. The dehydrogenation temperature of KBH_4 will be less under vacuum or inert gas flow conditions. The thermodynamic calculations have shown that the additive $ZrCl_4$ could chemically react with KBH_4 even at room temperature during ball milling. Therefore, XRD analysis of $cKBH_4$ has been performed and compared with the XRD result of $pKBH_4$ under similar ball milling conditions. The XRD results are presented in Fig. 2a–b. The XRD analyses of both the samples have shown single phase KBH_4. Although $ZrCl_4$ should chemically react with KBH_4 during ball milling and KCl would be one of the products, it has not been detected in the XRD even in the enlarged XRD pattern presented as an inset of Fig. 2. The result seems to be due to the insufficient fraction of KCl formed during the ball milling (<1% fraction could not be detected by conventional XRD). The FTIR analyses of ball milled $pKBH_4$ and $cKBH_4$ have been performed after

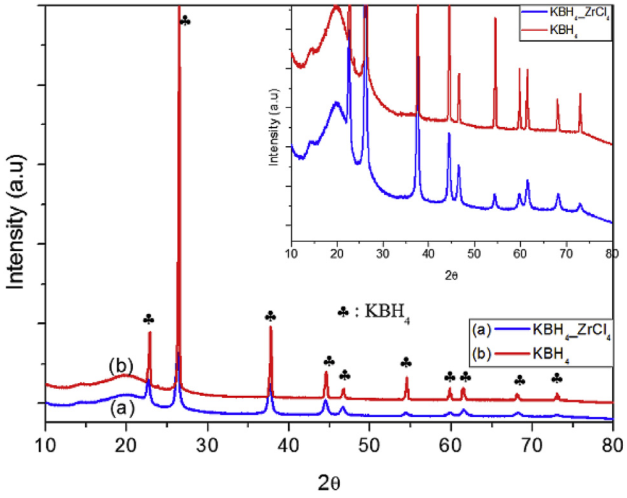

Fig. 2. The XRD analysis of (a) $cKBH_4$ (b) $pKBH_4$ after 2 h ball milling under argon atmosphere. The XRD patterns of both the samples were identical. The inset shows the enlarged figure to see if any secondary phase has been formed during the ball milling.