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$NaBH_4$ formation mechanism by reaction of sodium borate with Mg and H_2

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Abstract

It has been reported that sodium (potassium) borohydride can be formed by reaction of sodium (potassium) borate with Mg and hydrogen or magnesium hydride. However, few investigations on reaction mechanism have been reported. Here, we studied the $NaBH_4$ formation mechanism of $Mg + NaBO_2 + 2H_2 = NaBH_4 + MgO$ through morphology observations, structure and micro composition analyses. It was found that when heating the reactor to 400 °C, $NaBO_2$ particles were agglomerated with Mg particles and a $NaBO_2$ network was formed due to the sintering effect. With further heating the reactor, a porous product layer (composed of $NaBH_4$ and MgO) was formed on Mg particles. It was found that no matter whether Mg was hydrogenated or not, Mg could react with sodium borate and hydrogen to form sodium borohydride. Elevating the reaction temperature was of benefit to $NaBH_4$ formation. Higher $NaBH_4$ yield can be obtained by using partially hydrogenated then dehydrogenated Mg.

Keywords: Sodium borohydride formation mechanism; Magnesium; Magnesium hydride; Sodium borate; Reaction temperature

1. Introduction

Borohydrides are a group of compounds with high hydrogen contents. Recently they have been attracted more attentions as a hydrogen storage medium for hydrogen generation or as a fuel for the direct borohydride fuel cell (DBFC) due to their high hydrogen storage capacity. Many papers related to hydrogen generation from borohydrides [1–14] and the DBFC [15–26] have been published. Comparing with topics of hydrogen generation from borohydrides and the DBFC, few papers related to borohydride synthesis were published [27–32]. Recent progresses on hydrogen generation from borohydrides and the DBFC have been summarized in review articles [33–35].

Currently the price of sodium borohydride is about 55 $/kg. In order to enlarge borohydride applications for hydrogen generation and the DBFC, the cost reduction of the borohydride production is necessary. If the cost of borohydride production can be reduced to 0.55 $/kg, borohydride will be a powerful competitor as a hydrogen storage medium. Therefore, more detailed researches are needed on the development of new borohydride synthesis technology to effectively lower down the cost.

Sodium borohydride is usually synthesized from NaH and methyl borate, which was invented by Schlesinger et al. [36]:

$$4NaH + B(OCH_3)_3 = NaBH_4 + 3NaOCH_3 \quad (1)$$

Beside sodium hydride, alkali-earth metal or their hydrides have been used for reaction with $NaBO_2$ to prepare $NaBH_4$ [27–31,37]. However, the detailed reaction mechanism has not been reported. In this paper, we studied the $NaBH_4$ formation mechanism through a reaction of dehydrated sodium borate with Mg and hydrogen at 550 °C based on morphology observations, structure and micro composition analyses. Based on them, effects of magnesium hydrogenation and reaction temperature on sodium borohydride formation were investigated.

2. Experimental details

In this research, Mg powder (purity: 99.9%, <200 mesh), sodium borate powder (purity: 98%, <50 mesh) and hydrogen (purity: 99.99%) were used as the reactants. A diagram of test apparatus is illustrated in Fig. 1. Confirmation of sodium borohydride formation was conducted by XRD. The borohydride yield was determined by hydrogen consumption amount or iodimetric analysis [38].

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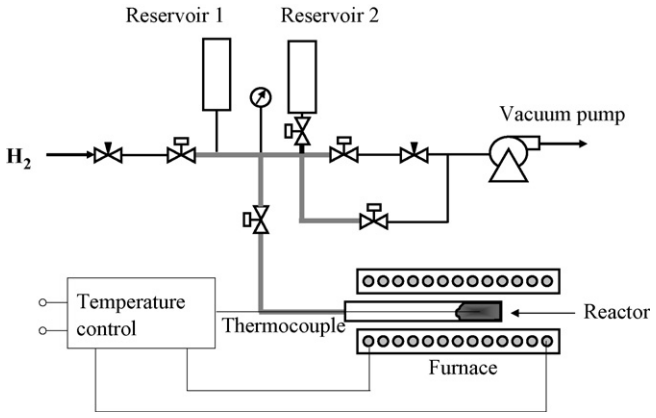

Fig. 1. Diagram of test apparatus for $NaBH_4$ formation.

The stoichiometric Mg powders and $NaBO_2$ powders were well mixed according to the following reaction:

$$NaBO_2 + Mg + 2H_2 = NaBH_4 + MgO, \quad \Delta G^\circ = -342\,kJ/mol\text{-}NaBH_4 \tag{2}$$

then put into a stainless steel reactor in which a thermocouple was placed in the reactant bed. The reactor was degassed during heating process before charge of hydrogen into the reactor. The hydrogen pressure was set at 3.1 MPa. Heating rate was 10 °C/min.

The samples were subjected to SEM, EPMA and XRD analyses at different stages of borohydride formation. The product ($NaBH_4$) was extracted by anhydrous ethylenediamine with a purity of 99%. Hardened filter paper was used to separate the extraction solution from formed oxides and remaining reactants. The solid product (white powder) was obtained by evaporating the extraction solution under 0.01 MPa at room temperature. A cold trap was applied to capture the solvent vapor (ethylenediamine) at −10 °C. The obtained powders were subjected to XRD analysis for qualitative identification of the borohydride formation. The amount of formed borohydride was quantitatively determined by iodimetric analysis.

To investigate the effect of Mg hydrogenation on borohydride formation, we did following experiments as shown in Fig. 2:

- Experiment 1: introduce hydrogen into the reactor after degassing the reactor at 25 °C, then heating the reactor to 550 °C.
- Experiment 2: introduce hydrogen into the reactor after degassing the reactor at 400 °C, and then heating the reactor to 550 °C.
- Experiment 3: introduce hydrogen into the reactor after degassing the reactor at 550 °C.

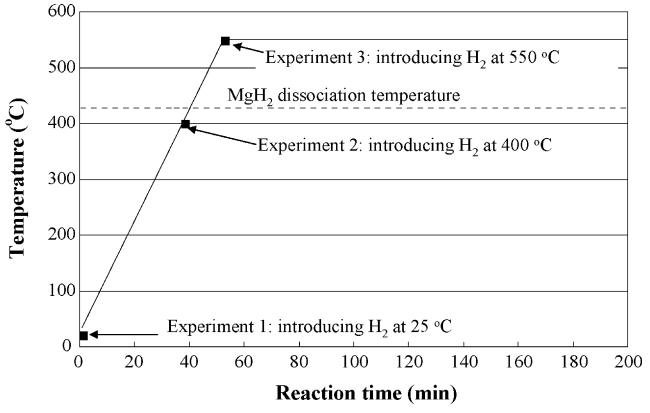

Fig. 2. Hydrogen introduction into the reactor at different temperatures. Hydrogen pressure, 3.1 MPa.

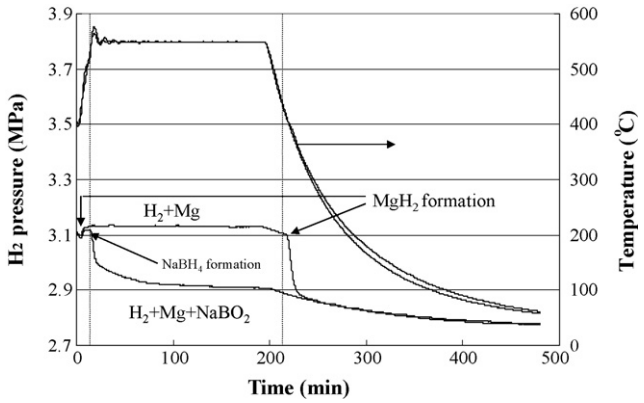

Fig. 3. Hydrogen consumption behavior during reaction of hydrogen with Mg or Mg + $NaBO_2$.

3. Results and discussion

3.1. Sodium borohydride formation

Fig. 3 shows the hydrogen consumption behaviors when hydrogen reacted with Mg or a mixture of Mg and $NaBO_2$. In both of the H_2 + Mg and the H_2 + Mg + $NaBO_2$ system, there was a small hydrogen pressure drop when heating the reactor from 400 to 426.8 °C. It can be attributed that MgH_2 formed according to Van't Hoff plot of Mg–H_2 system [39]. Because the heating rate was 10 °C/min, Mg only can absorb little hydrogen within 2.6 min. Then the hydrogen pressure of the system increased a little when heating reactor from 426.8 to 525 °C due to dehydrogenation of the formed MgH_2. In following processes, the H_2 + Mg and the H_2 + Mg + $NaBO_2$ system began to show different hydrogen consumption behaviors.

In the H_2 + Mg system, while the reactor was heated to 550 °C, then held at 550 °C for 185 min, no hydrogen pressure drop was found. The reactor was then cooled from

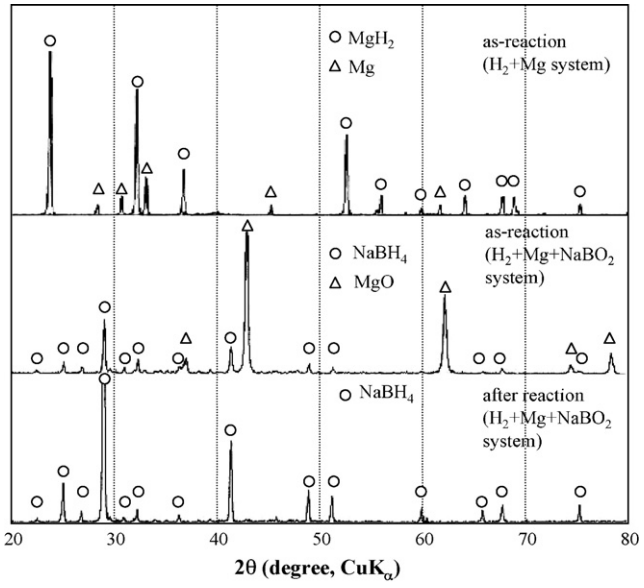

Fig. 4. Confirmation of $NaBH_4$ formation by XRD.

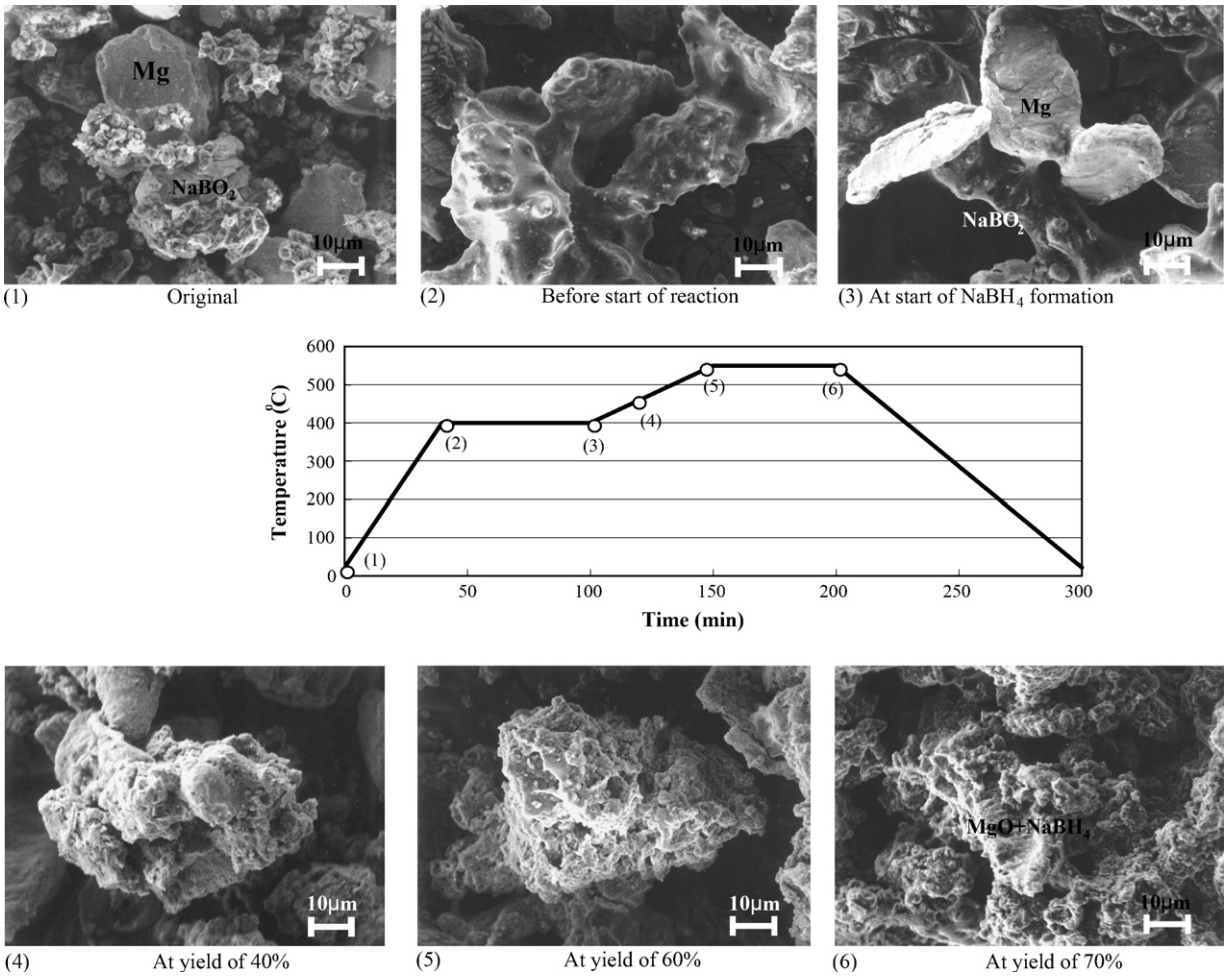

Fig. 5. SEM images in the process of $NaBH_4$ formation.

550 to 426.8 °C, the system hydrogen pressure was back to original pressure. In the following cooling process, the system showed a big drop in hydrogen pressure. It can be attributed that Mg began to absorb hydrogen because magnesium hydride formed below 426.8 °C at 3.1 MPa of hydrogen pressure according to Van't Hoff plot of Mg–H_2 system [39].

In the $H_2 + Mg + NaBO_2$ system, a big drop in hydrogen pressure occurred at 525 °C and hydrogen pressure kept decreasing in the following process of heating the reactor to 550 °C and holding the reactor at 550 °C for 185 min. It can be concluded that there were some hydrides formed at 525 °C, which were different from magnesium hydride.

The obtained samples from the $H_2 + Mg$ and the $H_2 + Mg + NaBO_2$ system were subjected to XRD analysis. The X-ray diffraction diagram verified the existence of MgH_2 in the $H_2 + Mg$ system and the existence of $NaBH_4$ and MgO in the $H_2 + Mg + NaBO_2$ system as shown in Fig. 4. It implied that $NaBO_2$ was converted to $NaBH_4$, and Mg was oxidized into MgO in the $H_2 + Mg + NaBO_2$ system. Fig. 4 gives the XRD result of the sample obtained from $H_2 + Mg + NaBO_2$ system after extraction with anhydrous ethylenediamine, filtration and drying. The XRD peaks clearly show the existence of $NaBH_4$. These results strongly proved that $NaBO_2$ reacted with Mg and H_2 to form $NaBH_4$ and MgO.

3.2. Morphology during $NaBH_4$ formation

Fig. 5 shows the morphology changes of Mg and $NaBO_2$ particles at each stage of the $NaBH_4$ formation. Particles were identified by EPMA through surface composition analyses (Na distribution and Mg distribution) as shown in Fig. 6. It can be seen that particles with smooth surfaces were Mg particles, and those with rough surfaces were $NaBO_2$. When heating the reactor to 400 °C, $NaBO_2$ particles were agglomerated with Mg particles and a $NaBO_2$ network was formed due to the sintering effect. While further heating the reactor, a porous product layer (composed of $NaBH_4$ and MgO) was formed on Mg particles. It was found that MgO and $NaBH_4$ were homogeneously distributed in the product layer as shown in Fig. 6(b-2) and (b-3). This porous layer was of benefit to the $NaBH_4$ formation because it would not be a barrier against hydrogen molecules to access to boundaries of Mg and $NaBO_2$. From our previous results as shown in Fig. 6 from (c-1) to (c-3) [30], there was

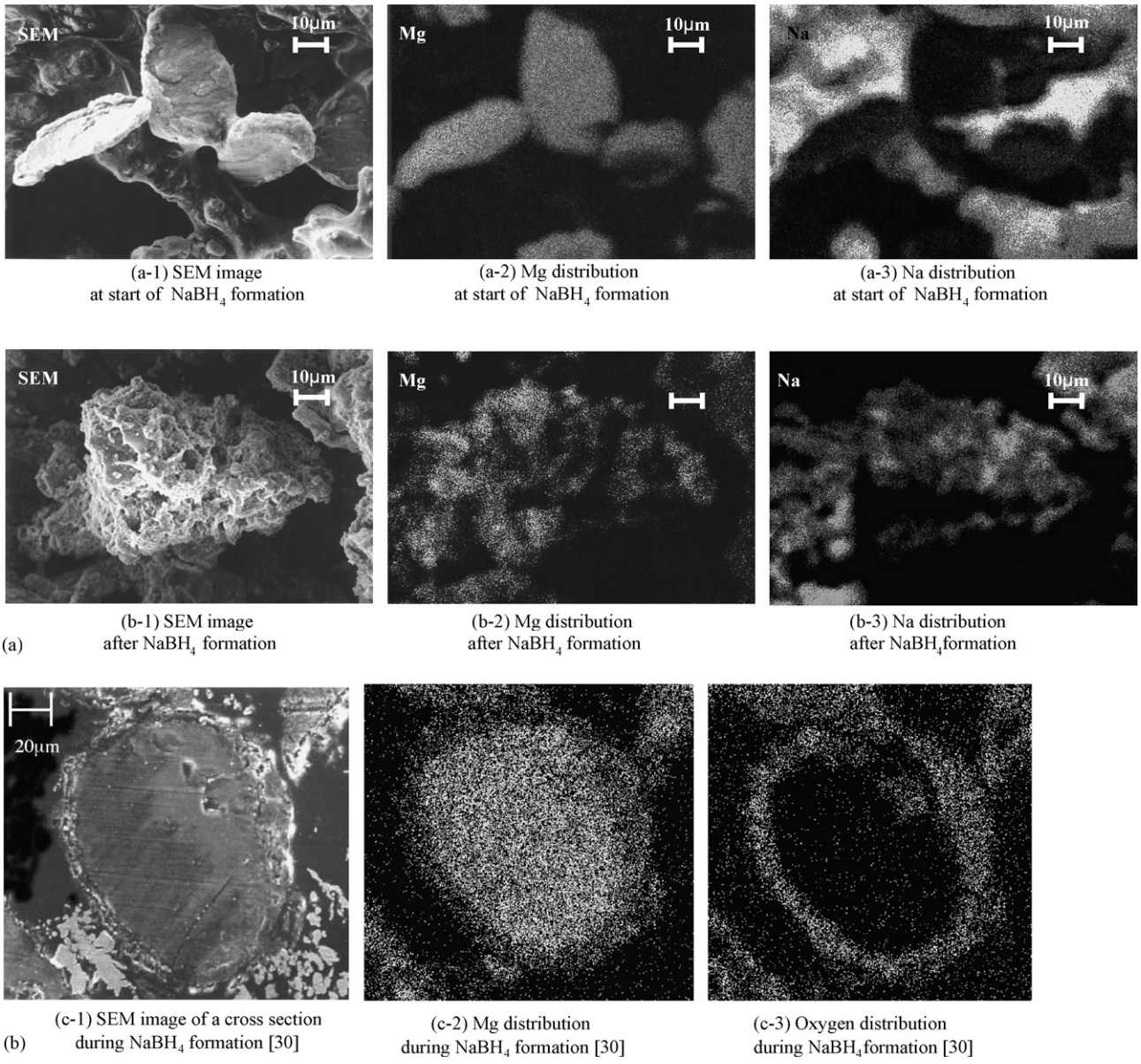

Fig. 6. Mg and Na distribution before and after $NaBH_4$ formation.

a clear boundary between the metallic Mg and the mixture of MgO and $NaBH_4$.

3.3. Effect of reaction temperature on $NaBH_4$ formation

Fig. 7 shows the relation of $NaBH_4$ yield vs. reaction temperature. Though reaction (2) is an exothermal reaction, $NaBH_4$ yield increased with elevating the reaction temperature. It implied that $NaBH_4$ formation was controlled by a mass diffusion process. Through morphology observations mentioned above, it can be speculated that the process of sodium borohydride formation would take place according to following steps:

(a) $NaBO_2$ particles were agglomerated with Mg particles at 400 °C, then form a $NaBO_2$ network, through which O^{2-} could diffuse to surfaces of Mg particles.

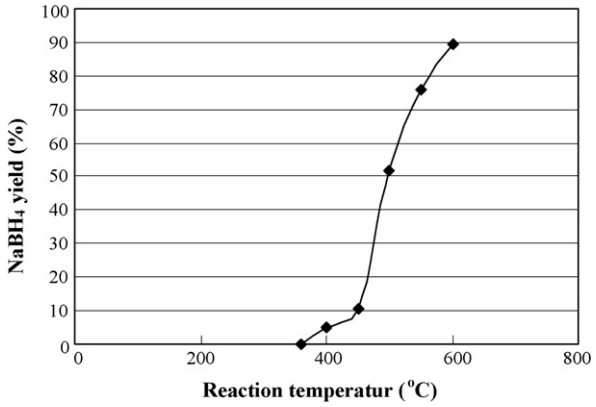

Fig. 7. $NaBH_4$ formation at different reaction temperatures.

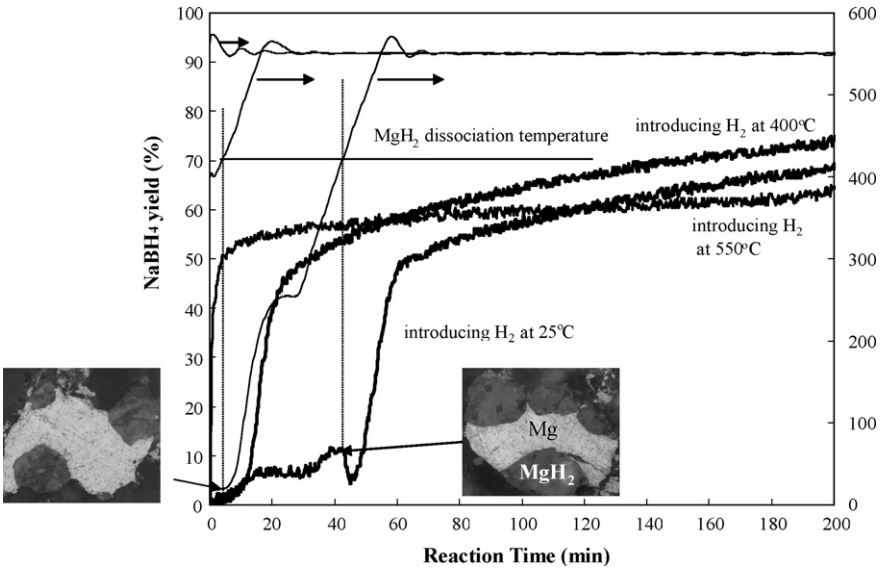

Fig. 8. $NaBH_4$ formation when introducing hydrogen into the reactor at different temperatures.

(b) O^{2-} from $NaBO_2$, invaded into metallic Mg lattice to leave vacancies in the $NaBO_2$ lattice.
(c) Hydrogen was dissociated to absorb on Mg surfaces.
(d) Mg was combined with O^{2-} to release two electrons to absorbed H on Mg surfaces.
(e) Absorbed H received electron to form H^-, and then move to the vacancies for combining with boron to form borohydride.

Elevating reaction temperature would be of benefit to O^{2-} diffusion in step (b), so that O^{2-} ions could deeply invade into metallic Mg lattice. Therefore, $NaBH_4$ yield increased with elevating the reaction temperature. Experimental results showed there was no $NaBH_4$ formed at 360 °C, but 4.8% of $NaBH_4$ yield was obtained at reaction temperature of 400 °C. It can be concluded that $NaBH_4$ formation temperature was located between 360 and 400 °C. Here, borohydride yield was determined by iodimetric analysis because magnesium hydride would be formed in this temperature range.

3.4. Effect of Mg hydrogenation on $NaBH_4$ formation

The start temperature of sodium borohydride formation was located at the temperature range of magnesium hydride formation. It implied that some magnesium hydrides would be formed during borohydride formation if reaction temperature was lower than MgH_2 dissociation temperature. Kojima et al. reported that higher $NaBH_4$ yield can be obtained by using MgH_2 as the reactant comparing with using Mg as the reactant [28]. However, from our previous results, it was found there was no Mg hydride existed during formation of $NaBH_4$ [30].

To find the role that Mg hydrogenation played during borohydride formation, we did following experiments as described in Section 2. In experiment 1, some magnesium hydrides were formed during heating the mixture of Mg and $NaBO_2$ from 25 to 426.8 °C under hydrogen (about 20 wt.% of Mg was hydrogenated), and then were dehydrogenated from 426.8 °C. In experiment 2, few magnesium hydrides were formed during heating from 400 to 426.8 °C within 2.6 min (about 2.5 wt.% of Mg was hydrogenated), and then were dehydrogenated from 426.8 °C. In experiment 3, no Mg was hydrogenated because the reactor temperature was higher than the magnesium hydride dissociation temperature.

Fig. 8 shows the $NaBH_4$ formation when introducing hydrogen into the reactor at different temperatures (experiments 1–3). The $NaBH_4$ yields were calculated from the hydrogen pressure drop. It was found that no matter whether Mg was hydrogenated or not, Mg could react with sodium borate and hydrogen to form sodium borohydride. Higher $NaBH_4$ yield can be obtained by using partially hydrogenated then dehydrogenated Mg. It might be attributed to that hydrogenation and dehydrogenation of Mg generated some defects in Mg particles so that O^{2-} ions could deeply invade into metallic Mg lattice through these defects. From Fig. 8, it was found that if the reactor temperature reached to reaction temperature of 550 °C more quickly, the $NaBH_4$ formation was faster. This result was coincidence with our previous conclusion that the rate of $NaBH_4$ formation was proportional to heating rate [31] and reconfirmed that the reaction temperature played an important role in $NaBH_4$ formation rate.

4. Conclusions

When heating the reactor to 400 °C, $NaBO_2$ particles were agglomerated with Mg particles to form a $NaBO_2$ network due to the sintering effect. $NaBH_4$ formation temperature was located between 360 and 400 °C. It was found that no matter whether Mg was hydrogenated or not, Mg could react with sodium borate and hydrogen to form sodium borohydride. $NaBH_4$ and MgO were formed on surfaces of Mg particles. $NaBH_4$ yield increased with elevating the reaction temperature. Higher $NaBH_4$ yield can be obtained by using partially hydrogenated then dehydrogenated Mg.

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