$NaBH_4$ Formation Through $NaBO_2$ Reacts with Mg and H_2

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Abstract: The effects of temperature, hydrogen pressure and catalyst addition on sodium borohydride formation were investigated. Higher H_2 pressure is of benefit to $NaBH_4$ formation. Increasing reaction temperature can improve $NaBH_4$ formation kinetic property. However, if the temperature is near the melting point of Mg, the $NaBH_4$ formation was impeded. Ni, Fe and Co addition in the H_2 + Mg + $NaBO_2$ system promoted the $NaBH_4$ formation, but Cu addition showed a negative effect.

Key words: sodium borohydride formation; kinetic property; catalyst; reaction temperature; hydrogen pressure
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Recently borohydrides have been attracted more attention as a hydrogen storage medium due to their high hydrogen storage capability. $NaBH_4$ contains 10.6% hydrogen. Furthermore, the hydrolysis of borohydride is of interest in hydrogen generation because half of the generated hydrogen is from the borohydride and the other half is from water. However, there were only few researches related to borohydride formation. It was reported that sodium borohydride can be formed by reaction of $NaBO_2$ with Mg and hydrogen (or MgH_2) through following reaction around 450 ℃[1-3]:

$$NaBO_2 + 2Mg + 2H_2 = NaBH_4 + 2MgO \quad (1)$$

Our previous results have proved that $NaBH_4$ can be formed from sodium meta-borate and magnesium hydride through ball milling at room temperature[4]. It was thought that reaction kinetic issue was important to the $NaBH_4$ synthesis.

The influences of temperature and hydrogen pressure on sodium borohydride formation were investigated. It was thought that the kinetic property of $NaBH_4$ formation might be improved by adding some catalysts in the H_2 + Mg + $NaBO_2$ system. We investigated the effect of Fe, Co, Ni and Cu addition on the $NaBH_4$ formation kinetic property.

1 Experimental details

Stoichiometric Mg powders and $NaBO_2$ powders according to reaction (1) were well mixed then were 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 at 400 ℃. Then the reactor was heated to the reaction temperatures at a heating rate of 10 ℃/min. $NaBH_4$ formation kinetic properties were investigated under 1.0 ~ 3.0 MPa of hydrogen pressure, 500 ~ 650 ℃ of reaction temperature.

2 Results and discussion

Fig. 1 shows the influence of reaction temperature and hydrogen pressure on the $NaBH_4$ formation. It was found that when the reaction temperatures were lower than 600 ℃, $NaBH_4$ formation rate and yield increased

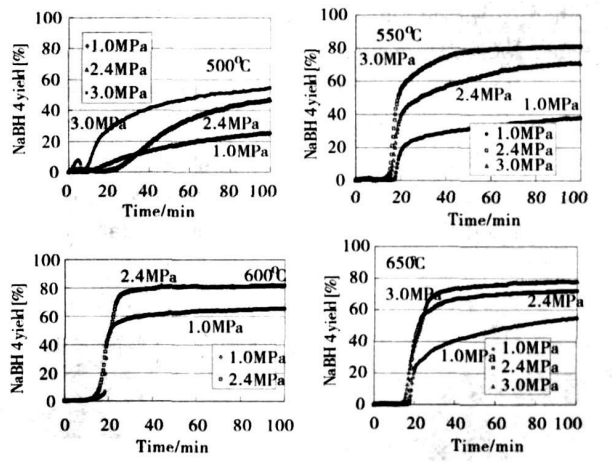

Fig. 1 Temperature and hydrogen pressure effects on $NaBH_4$ formation

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with increasing reaction temperature. However, when the reaction temperature reached up to 650 ℃, $NaBH_4$ formation rate and yield were decreased. At 650 ℃, local melting phenomenon of the reaction bed would occur, because the reaction temperature was close to the melting point of Mg (651 ℃). The molten Mg would fill into the micro holes in the reaction bed. As a result the diffusion of the hydrogen gas to the interfaces of Mg and sodium meta-borate particles would be impeded. Therefore, $NaBH_4$ formation rate and yield were decreased. Higher H_2 pressure generally was of benefit to $NaBH_4$ formation as shown in Fig. 1. It can be seen that high H_2 pressure could improve the $NaBH_4$ formation even near Mg melting point. All these results can be attributed to that the diffusion of the hydrogen gas to the interfaces of Mg and sodium meta-borate particles can be improved by increasing the H_2 pressure in the $H_2+Mg+NaBO_2$ system.

Fig. 2 shows effects of Ni, Co, Fe and Cu addition on the $NaBH_4$ formation and kinetic properties. According to our pervious observation to the formation of $NaBH_4$ and MgO[2-3], it was found that the formed layer of $NaBH_4$ and MgO from reaction (1) was similar to the image of the Mg hydride layer during Mg hydrogenation. When Fe was introduced into the $H_2+Mg+NaBO_2$ system, not only $NaBH_4$ formation temperature was lowered, but also $NaBH_4$ yield was improved. It implied that Fe addition lowered the nucleation energy of $NaBH_4$ formation so that reaction (1) could occur at lower temperature. Furthermore, Fe addition would promote growth of the product layer ($NaBH_4+MgO$). When Ni was introduced into the $H_2+Mg+NaBO_2$ system, $NaBH_4$ formation temperature was further lowered. It implied that Ni addition can further decrease the nucleation energy, though the $NaBH_4$ yield was decreased a little. It is because Ni has higher catalytical property than Fe. When Co was introduced into the $H_2+Mg+NaBO_2$ system, $NaBH_4$ formation rate was improved, but $NaBH_4$ formation temperature was kept the same. It implied that Co addition improved the growth of the product layer ($NaBH_4+MgO$).

From above results, it was clear that Ni, Fe and Co addition were of benefit to $NaBH_4$ formation though it is hard to tell the detailed mechanism at recent stage. However, unlike Ni, Fe and Co addition, Cu addition impeded the $NaBH_4$ formation. It might attributed to that Cu is lack of empty out d-electron orbit for electron exchange due to its out electron orbit $3d^{10}4s^1$ which is different from $3d^64s^2$ of Fe, $3d^74s^2$ of Co and $3d^84s^2$ of Ni.

4 Conclusions

Higher H_2 pressure is of benefit to $NaBH_4$ formation. Increasing reaction temperature can improve $NaBH_4$ formation. However, if the temperature is near the melting point of Mg, the $NaBH_4$ formation will be impeded. Ni, Fe and Co addition in the $H_2+Mg+NaBO_2$ system can promote the $NaBH_4$ formation, but Cu addition shows a negative effect.

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偏硼酸钠与镁和氢反应的硼氢化钠生成

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摘 要: 高的氢压和反应温度有利于片硼酸钠与镁和氢反应生成硼氢化钠, 但温度接近镁的熔点时不利于硼氢化钠的生成。在反应物中添加铁、镍和钴将加速硼氢化钠的生成, 而铜的加入却阻碍硼氢化钠的生成。

关键词: 硼氢化钠生成; 动力学特性; 催化剂; 反应温度; 氢压

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