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Study on catalyst for the sodium borohydride hydrolysis

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Abstract: The effects of preparation methods, supports and active parts on both the activation and stability of catalyst for the sodium borohydride hydrolysis were studied, and the results showed that the activation and stability of the catalysts prepared by impregnation method is better than that prepared by chemical plating. Compared to exchange resin and activated alumina, the diatomite with high BET surface area and porosity is more suitable for as the catalyst's support. Co is much better than Ni when used as catalytic active part.

Key words: sodium borohydride; catalyst; catalytic activation; stability

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1 Introduction

As an important part in the new energy sources, hydrogen energy technologies include the H₂ generation, storage and application. The hydrogen storage is the key step^[1]. People pay more and more attention to the chemical hydrogen storage technology due to its high hydrogen storage rate, safe and stable application.

Sodium borohydride (NaBH₄) is a complex hydride. When sodium borohydride is used to store hydrogen, and its hydrogen storage capacity is theoretically about 10.8 % (mass fraction)^[2].



The hydrolysis reaction is exothermic, if it reacts with water directly and acutely, the hydrogen production will be out of control. Accordingly, the sodium borohydride catalyzed hydrolysis technology is the emphasis in this field. By this technology, the sodium borohydride hydrogen production process is under control. The catalysts are the key in sodium borohydride catalyzed hydrolysis technology. Steven C found the Ru-anion exchange resin catalyze the sodium borohydride hydrolysis evidently^[3]. Jin-Ho Kim found that the filamentary Ni prepared by a paste method can also catalyze the reaction^[4]. Yoshitsugu Kojima investigation showed that the hydrogen generation rate of Pt-LiCoO₂ prepared by the conventional impregnation method is much better than that of Ru-IRA400 resin^[5]. Since the sodium borohydride solution is hydrolyzed on the surface of the catalyst, the high surface rate is very important for improving the hydrolyzed rate. The support can provide the high surface area and appropriate pores, and enhance the active part's efficiency. Therefore, in this paper some supported catalysts were prepared, and the effect of supports types

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and active parts on the catalyst's properties were studied.

2 Experimental

2.1 Catalysts supports and active parts

Activated carbon, activated alumina, anion exchange resin and diatomite with high surface area were selected as the catalyst's supports. Nickel and cobalt were selected as the active parts of catalyst.

2.2 Preparation method of catalyst

2.2.1 Impregnation

Firstly, the supports was dipped in the alcohol for half an hour to clean it, and then it was dried at 60°C in vacuum for four hours. After that, the support was dipped into the Ni or Co saline solution for 20 min, and then

filtrated, dried, deoxidized and cleaned. Lastly, the catalyst was dried at 90°C in vacuum for five hours.

2.2.2 Chemical plating

The supports were pretreated before chemical plating. The pretreated process was as follows: alkaline degreased in the Na_3PO_4 solution, roughened in the HF solution, sensitized in the SnCl_2 solution, activated in PbCl_2 solution and reduced in the NaH_2PO_2 solution. After that, the supports were dipped into the Ni or Co saline solution for chemical plating.

2.3 Catalytic activation test

Testing solution is 5 g/L sodium borohydride and 20 g/L sodium hydroxide solution. The reacting temperature is 30°C. Hydrogen production volume is collected by draining water in constant time alternation for plotting hydrogen volume-time curve. The catalytic ability can be obtained by calculating the slope of the hydrogen volume-time curve and the mass of the catalyst.

3 Results and discussion

3.1 Active parts selecting

Fig. 1 shows the activation test results of the Ni and Co catalysts, respectively, prepared on the anion exchange resin, diatomite and activated carbon by impregnation method. It can be seen that the activation of Co catalyst is higher than that of Ni on the same support. This conclusion accords with the report of the reference [7].

3.2 The supports selecting

Fig. 2 shows the activation of Co catalysts prepared on different supports by impregnation method. It can be seen that the activation of Co catalysts prepared on diatomite and anion exchange resin is higher than that prepared on other supports, due to the light and high surface area of diatomite and anion exchange resin.

In the catalyst recycling, the resin support is better than the diatomite. However, the resin is unsteady when it is in an alkaline solution. Fig. 3 shows the surface microstructure of Co-resin catalyst before and after its using. It can be seen that the original resin is in a glazed ball shape. After dipped in cobalt salt

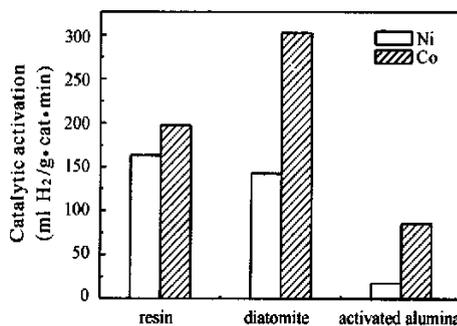


Fig. 1 Activation of Ni and Co catalysts prepared on the different supports

solution and reduced in the sodium borohydride solution, the resin is partly broken. When it is continually dipped in the alkaline solution for five days, more and more resin are seriously broken. One reason is that the mechanical property of the resin is bad. The other one is that when the resin is dipped in the alkaline solution for a long term, the functional group of resin is substituted by the $-OH$ of the solution, and then the resin's mechanical property is worsen.

Compared to the resin, the diatomite has a high porosity, high surface area, low density, good anticorrosion performance and high thermo-stability, and adhesion strength between Co plant and support can be obviously improved by the heat treatment. Therefore, the diatomite is more suitable for as the catalyst's support.

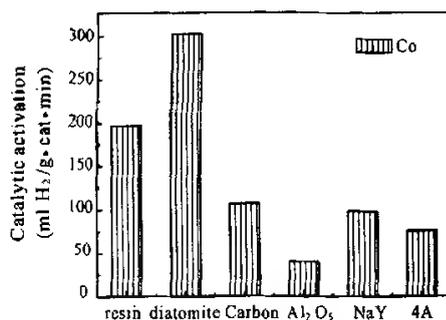


Fig. 2 Activation of Co catalysts prepared on the different supports

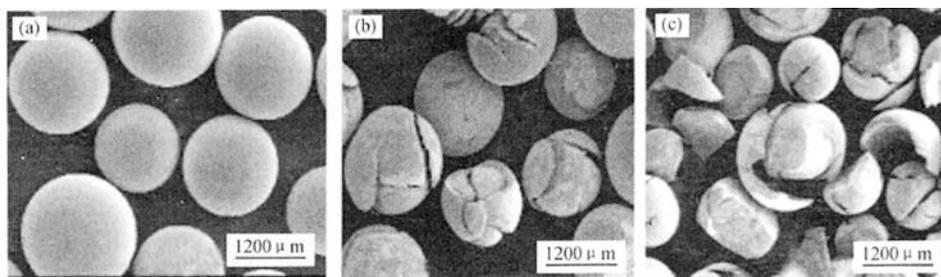


Fig. 3 Microstructure of Co-resins catalyst

(a) — original resin; (b) — Co-resin catalyst; (c) — after dipped in alkali solution for 5 days

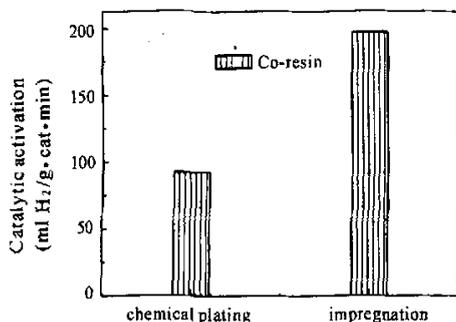


Fig. 4 Activation of Co-resin catalyst prepared by chemical plating and impregnation, respectively

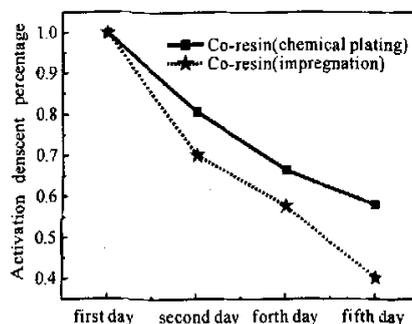


Fig. 5 Stabilization of Co-resin catalyst prepared by chemical plating and impregnation, respectively

3.3 Selection for catalysts preparation method

Fig. 4 and Fig. 5 show the activation and stabilization of Co-resin catalyst prepared by impregnation and chemical plating, respectively. It can be seen that the stabilization of the Co-resin catalyst prepared by chemical plating is better than that prepared by impregnation method, but its activation is lower than the latter.

Fig. 6 shows the surface photograph of Co-resin prepared by the impregnation and chemical plating

methods, respectively. As seen in Fig. 6, the surface of Co-resin catalyst prepared by the chemical plating is glazed, so the catalyst's surface area is small and original activation is low. Moreover, the plate is thin and much support's surface was not covered by Co plate.

Compared with the Co-resin catalyst prepared by chemical plating, there is much protuberance on the surface of the catalyst prepared by impregnation. So the surface area of catalyst prepared by impregnation method is large. In addition, the support's surface is nearly all covered by Co. Therefore, catalyst's original activation is high.

During the stabilization of catalyst test, it is found that after catalyst hydrolysis reaction the solution's color changed to brown due to the Co peeling off from the support, which indicates that the chemical plating method did not improve the adhesion strength between the Co plate and support. Therefore, in consideration of the activation and stabilization of catalyst, the impregnation method is suitable for preparing the catalyst.

4 Conclusions

(1) Compared to the resin and activated alumina, the diatomite has high surface area and high anticorrosion properties, so it is more suited to the catalyst's support.

(2) The activation of Co catalyst is higher than that of Ni catalyst, so Co is more suitable for acting as the active part of catalyst.

(3) The activation and stabilization of catalyst prepared by impregnation is high than that of prepared by chemical plating.

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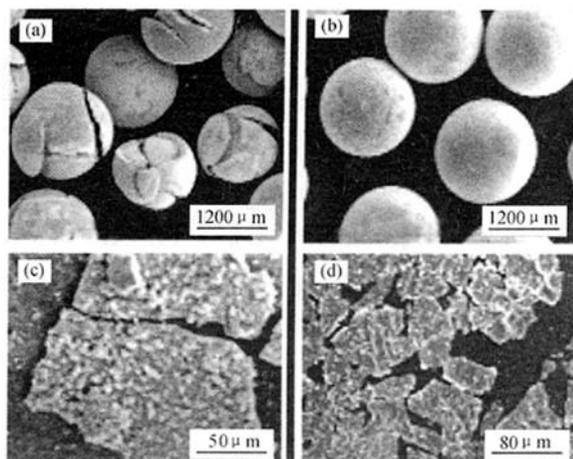


Fig. 6 Surface photographs of Co-resin catalyst
(a), (c)—catalysts prepared by impregnation method; (b),
(d)—catalysts prepared by chemical plating