

SODIUM BOROHYDRIDE FOR HYDROGEN STORAGE

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Introduction

It is known, that sodium borohydride NaBH_4 is the extremely hygroscopic matter actively absorbing moisture. Water solutions of NaBH_4 always contain some sodium hydroxide NaOH generated by partial hydrolysis of NaBH_4 . In an aqueous medium the hydrolysis of NaBH_4 occurs with gradual deceleration owing to increase of pH of a solution during the process and the behavior of water solutions of NaBH_4 is characterized by the properties of triple system $\text{NaBH}_4\text{-NaOH-H}_2\text{O}$. Some data on stability of alkaline borohydrides in water and alkali solutions are currently available [1-3]. But these researches were conducted for highly weak solutions.

This paper examines the storage stability of NaBH_4 , either in forms of strong solutions or solid composition corresponding to NaBH_4 crystalline hydrate.

Experimental set up

Stability properties of aqueous solutions of NaBH_4 and its decomposition rate were studied in stainless steel cylindrical vessel with flanged cover.

The flange has tetrafluorethylene seal and equipped with Swagelok fitting to connect a precise manometer. The vessel filled with the solution to be studied was placed to liquid thermostat. Time variation of decomposition rate of sodium borohydride was estimated using measured values of gas pressure inside the vessel. This value is proportional to amount of hydrogen produced.

Experimental values of decomposition rate were corrected using value of hydrogen loss at period between the end of solution preparation and final pressurization of the test vessel. This correction is essential in the case of highest test temperatures and highly diluted solutions of NaBH_4 . The correction was based on measured steady-state values of decomposition rate.

Results and discussion

The study on stability of a triple $\text{NaBH}_4\text{-H}_2\text{O-NaOH}$ system were made for NaBH_4 concentration range 7-42 %, alkali concentration 1.5-6 % and temperature from 0 up to 50°C.

The decomposing of NaBH_4 in aqueous-alkali solutions goes much more slowly, than in pure water; the stability of such solutions increases with its alkalinity (Fig.1).

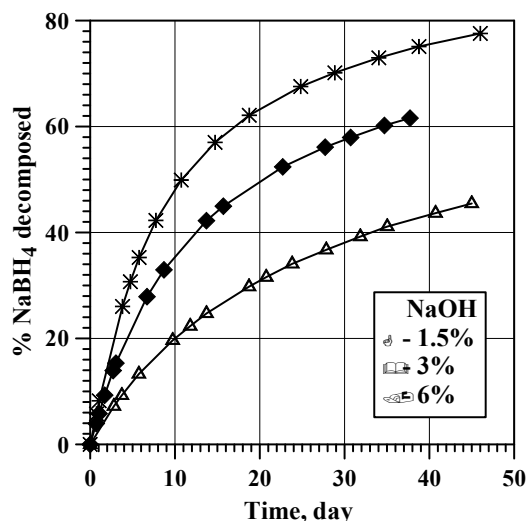


Fig.1. Hydrolysis of NaBH_4 in alkali solution of NaOH at 50°C. $C_{\text{NaBH}_4} = 19.8\%$.

An increase of NaBH_4 concentration and decrease of temperature makes the solution more stable (Fig.2). The addition of alkali solution to the composition slows down the hydrolysis process, but stabilizing efficiency of alkali reduces with temperature growth (Fig.2. curves 1,3).

At preparing of water compositions with NaBH_4 concentration higher than 50% porous particles are produced. After drying at room temperature these particles transform to free-flowing coarse-dispersed powder. A number of powders of following composition $\text{NaBH}_4\cdot\text{H}_2\text{O}$, $\text{NaBH}_4\cdot 1.4\text{H}_2\text{O}$, $\text{NaBH}_4\cdot 2\text{H}_2\text{O}$ (crystalline hydrate form of sodium borohydride) were prepared and its stability in temperature range 30-50°C was studied.

At temperature above 36.4°C (as it follows from dissolubility polytherms of binary $\text{NaBH}_4\text{-H}_2\text{O}$ system) and irrespective of hydrating rate of NaBH_4 molecule the powder "melts down" and this process is accompanied by hydrogen emission.

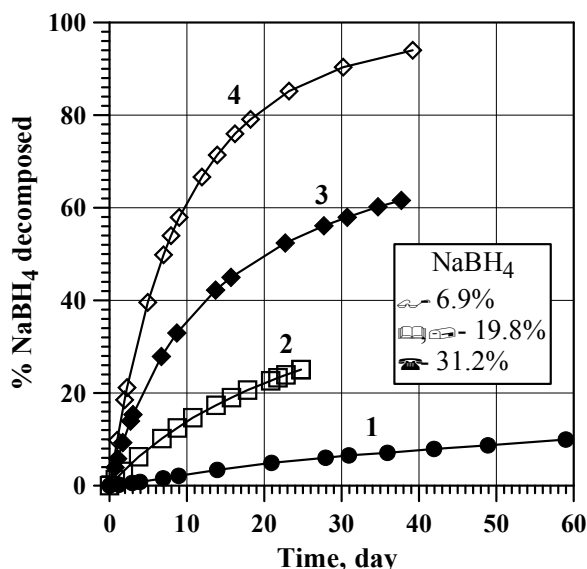


Fig.2. Hydrolysis of NaBH₄ in 3% solution of NaOH at 22°C (curve 1) and at 50°C (curves 2-4).

The addition of alkali results in stabilization of NaBH₄ crystalline hydrate. When the NaBH₄ concentration is higher than 51.2% and temperature is below 36.4°C the system NaBH₄-H₂O-NaOH is in a solid state in form of mixture of NaBH₄·2H₂O and NaBH₄ and hydrolysis of NaBH₄ is absent.

In figures 3-4 the time variation of NaBH₄ decomposition rate for the NaBH₄·2H₂O-NaOH system in temperature range 40-60°C and alkali concentrations 0-3 % are presented.

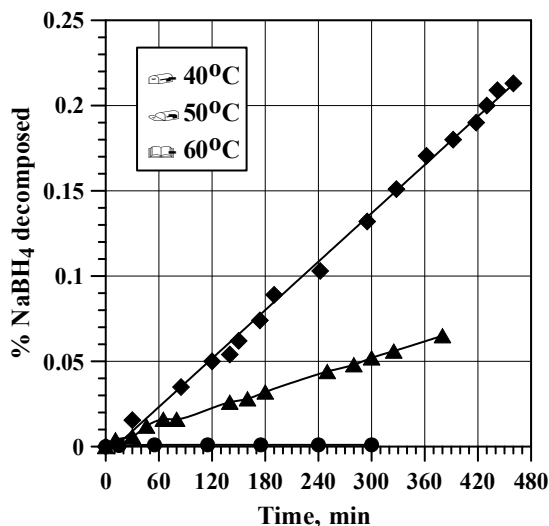


Fig.3. Temperature effect on decomposing of NaBH₄ for the NaBH₄·2H₂O-3%NaOH system

At high concentration of caustic NaOH equal to 3 % and at operating temperature equal to 40°C no hydrogen emission during experiment is observed, but at temperatures above 40°C slow hydrolysis of sodium borohydride takes place (Fig.3).

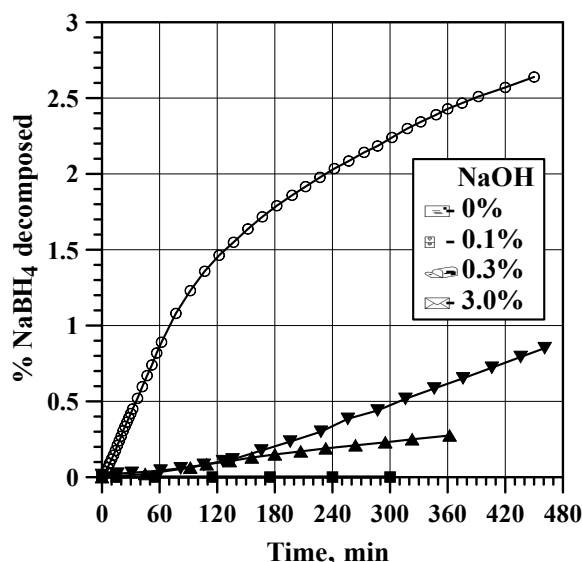


Fig.4. Influencing of input concentration of NaOH on decomposing of NaBH₄ at 40°C for the system NaBH₄·2H₂O-NaOH

Thus, our experimental data show that alkali addition cannot help to stop NaBH₄ hydrolysis reaction completely at temperatures above 40°C for crystalline hydrate and at any temperatures for solutions.

Conclusion

The result of present study is, that triple NaBH₄-H₂O-NaOH systems, obtained on the basis of crystalline hydrate of sodium borohydride with addition of a small amount of alkali have a high enough stability which is an order of magnitude exceed the similar triple systems in solution.

It is expedient to store sodium borohydride in the form of dry crystalline hydrate (with small addition of alkali). This matter is stable at temperatures below 36.4°C, has better mechanical properties and better solubility, in comparison with anhydrous NaBH₄.

References

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