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Kinetic modeling of self-hydrolysis of aqueous NaBH₄ solutions by model-based isoconversional method

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ABSTRACT

The present work reports the kinetic modeling of self-hydrolysis of non-buffered, non-stabilized NaBH₄ solutions by model-based isoconversional method. The overall kinetics is described by a 'reaction-order' model in a practical operating window of 10–20 wt% NaBH₄ solutions at 25–80 °C and 0–50% conversions. The apparent activation energy and pre-exponential factor are interrelated through a kinetic compensation effect (KCE). The apparent reaction order remains constant at a given temperature irrespective of extent of conversion and decreases with increase in temperature. It decreases from first-order to 0.26 with increase in temperature from 25 to 80 °C. The apparent activation energy is found to increase from 65 ± 11 to 162 ± 2 kJ mol^{-1} with increase in extent of conversion from 0 to 50%. The variation of parameters with extent of conversion is discussed based on changes in solution properties during the progress of hydrolysis reaction.

Introduction

Sodium borohydride (NaBH₄) undergoes self-hydrolysis in the presence of water while generating hydrogen according to [1–3]:

$$NaBH_4(s) + (2+x)H_2O(l) \rightarrow NaBO_2 \cdot xH_2O(aq \text{ or } s) + 4H_2(g) + heat \qquad (1)$$
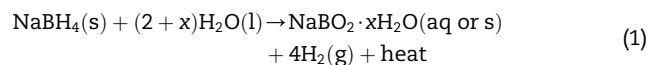
where x is the excess hydration factor [2].

The overall conversion of this reaction at room temperature is 7–8% [4,5], making it inappropriate for a practical H₂ generator. Certain metal catalysts accelerate the reactant conversion and metal-catalyzed hydrolysis is being accepted as a potential technology for delivering H₂ to portable fuel cells [6–9]. While the conversion of NaBH₄ is accelerated by metal-catalyzed hydrolysis, self-hydrolysis still occurs to some extent at low temperatures and becomes significant at elevated temperatures. This needs to be arrested for increasing the shelf-life of the reactant solution [10–14].

There are also unresolved issues such as the minimization of the amount of water and the nature of hydration of metaborate by-products which limit the net or usable hydrogen storage capacities [2]. An alternative method, steam

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